Società Chimica Italiana

SCI2021

XXVII CONGRESSO NAZIONALE DELLA SOCIETÀ CHIMICA ITALIANA

LA CHIMICA GUIDA LO SVILUPPO SOSTENIBILE

14–23 SETTEMBRE 2021

FAR – FIS – IND

BOOK OF ABSTRACTS
XXVII congresso della SCI, 2021

La chimica guida lo sviluppo sostenibile
14-23 settembre 2021

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Benvenuti a SCI2021!

Il Congresso Nazionale della Società Chimica Italiana, giunto alla sua XXVII edizione, si svolgerà in modo virtuale da martedì 14 settembre a giovedì 23 settembre 2021. Come di consueto, sarà un punto di incontro e di confronto per tutto il mondo della chimica in Italia su argomenti di grande attualità.

Il congresso sarà aperto dalla ***plenary lecture*** **del Prof. Stanley Whittingham, premio Nobel per la Chimica 2019**, e prevede interventi di una serie di illustri oratori, fra cui **il premio Nobel per la Chimica 1981, Prof. Roald Hoffmann**. Il congresso si articolerà in sessioni plenarie di interesse generale e sessioni parallele, a cura delle Divisioni della Società Chimica Italiana. Nel pomeriggio di mercoledì 22 settembre sono previsti eventi satellite di interesse industriale, accessibili gratuitamente per gli iscritti al congresso.

Nelle attuali necessità di distanziamento sociale, il congresso si svolgerà tutto in modalità live telematica, con presentazioni, discussioni e tavole rotonde in diretta. Gli interventi verranno comunque registrati e resi disponibili ai partecipanti nelle due settimane successive alla chiusura del congresso, con possibilità di contatto e discussione con i presentatori.

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COMITATO SCIENTIFICO

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DELEGATI DI DIVISIONE

CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI

Ezio Bolzacchini	ezio.bolzacchini@unimib.it
Lucia Toniolo	lucia.toniolo@polimi.it

CHIMICA ANALITICA

Marco Orlandi	marco.orlandi@unimib.it
Patrizia Mussini	patrizia.mussini@unimi.it

CHIMICA FARMACEUTICA

Paola Conti	paola.conti@unimi.it
Giulio Vistoli	giulio.vistoli@unimi.it

CHIMICA FISICA

Elena Selli	elena.selli@unimi.it
Moreno Meneghetti	moreno.meneghetti@unipd.it

CHIMICA INDUSTRIALE

Ilenia Rossetti	ilenia.rossetti@unimi.it
Antonella Salvini	antonella.salvini@unifi.it

CHIMICA INORGANICA

Emma Gallo	emma.gallo@unimi.it
Francesco Ruffo	francesco.ruffo@unina.it

CHIMICA ORGANICA

Alessandro Abbotto	alessandro.abbotto@unimib.it
Andrea Pace	andrea.pace@unipa.it

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DELEGATI DI DIVISIONE

CHIMICA DEI SISTEMI BIOLOGICI

Jussara Amato jussara.amato@unina.it
Danilo Milardi danilo.milardi@cnr.it

DIDATTICA CHIMICA

Ugo Cosentino ugo.cosentino@unimib.it
Sergio Palazzi studio@kemia.it

ELETTROCHIMICA

Luigi Falciola luigi.falciola@unimi.it
Riccardo Ruffo riccardo.ruffo@unimib.it

SPETTROMETRIA DI MASSA

Giuseppe Paglia beppepaglia@gmail.com
Matteo Audano matteo.audano@unimi.it

CHIMICA TEORICA E COMPUTAZIONALE

Michele Ceotto michele.ceotto@unimi.it
Claudio Greco claudio.greco@unimib.it

CHIMICA PER LE TECNOLOGIE

Alessandro Sacchetti alessandro.sacchetti@polimi.it
Fabio Ganazzoli fabio.ganazzoli@polimi.it

TECNOLOGIA FARMACEUTICA

Nunzio Denora nunzio.denora@uniba.it
Rosario Pignatello rosario.pignatello@unict.it

XXVII Congresso Nazionale della Società Chimica Italiana
"SCI 2021", 14-23 settembre 2021

	14 settembre	15 settembre	16 settembre	17 settembre
09:30-10:30		**Lavori Divisioni** **14 Sessioni Parallele** **1 (ABC) + 2 (FAR) + 2 (FIS) + 3 (INO) + 2 (TEC) + 3 (ELE) + 1 (TFA)**	**Lavori Divisioni** **14 Sessioni Parallele** **3 (ANA) + 3 (FIS) + 2 (IND) + 3 (ORG) + 1 (CSB) + 1 (ELE) + 1 (TEC)**	**Lavori Divisioni** **14 Sessioni Parallele** **2 (ABC) + 2 (FAR) + 2 (FIS) + 3 (INO) + 1 (TEC) + 3 (ELE) + 1 (TFA)**
10:30-11:00				
11:00-11:30				
11:30-12:00				
12:00-12:30			Break	
12:30-13:00			**ASSEMBLEE DIVISIONALI** **14 sessioni parallele** **(12:30 - 14:45)**	
13:00-14:00		Break		Break
14:00-14:30		ePoster Session		ePoster Session
14:30-15:00				
15:00-16:00	**APERTURA DEL CONGRESSO** *Saluti* **Maria Cristina MESSA** Ministro del MUR **Maria Chiara CARROZZA** Presidente CNR **Plenary Lecture del Prof. Stanley WHITTINGHAM** **PREMIO NOBEL PER LA CHIMICA 2019** Binghamton University, State University of New York, USA	**Lavori Divisioni** **14 Sessioni Parallele** **3 (ANA) + 2 (FAR) + 1 (IND) + 4 (ORG) + 1 (CSB) + 1 (DID) + 1 (MAS) + 1 (TEO)**	Sessione plenaria 2 ***La Chimica per il Benessere e la Qualità della Vita*** **Gunda I. GEORG** University of Minnesota, Department of Medicinal Chemistry, USA	**Lavori Divisioni** **14 Sessioni Parallele** **3 (ANA) + 1 (IND) + 1 (ABC) + 4 (ORG) + 1 (CSB) + 1 (DID) + 1 (MAS) + 2 (TEO)**
16:00-16:30	Sessione plenaria 1 ***Chimica, la Scienza al Centro***		**Juliane HOLLENDER** Swiss Federal Institute of Aquatic Science and Technology	
16:30-17:00	**PREMIAZIONE DELLE MEDAGLIE SCI 2020**		**Luis Liz MARZAN** CIC biomaGUNE, San Sebastián, Spain	
17:00-:17:30	Break		**Patrick COUVREUR** Université Paris-Sud France	
17:30-18:00	***Elsevier's Lecture*** **Ralf METZLER** Theoretical Physics, University of Potsdam, Germany		**Mark NOE** vice-Presidente della Pfizer	
18:00-18:30	Live Q&A Sessione 1	Discussione	Live Q&A Sessione 2	Discussione
18,30-19,30	ePoster	e-poster	e-poster	e-poster

	20 settembre	21 settembre	22 settembre	23 settembre
09:30-10:30	**Lavori Divisioni** **3 Sessioni Parallele**	**Lavori Divisioni** **14 Sessioni Parallele**	Gruppo Giovani **Yan LIANG** University of Science and Technology of China	**Lavori Divisioni** **13 Sessioni Parallele**
10:30:11:00	**3 (ORG)**	**2 (ABC) + 2 (FAR) + 2 (FIS) + 3 (INO) + 1 (TEC) + 3 (ELE) + 1 (TFA)**		**3 (ANA) + 3 (FIS) + 1 (IND) + 3 (INO) + 3 (ORG)**
11:00-11:30			**2 Sessioni Parallele**	
11:30-12:30				
12:30-13:00	**Break**			

13:00-14:00	**ASSEMBLEA GENERALE (13:00 - 14:45)**	Break	Break	Break
14:00-15:00		ePoster Session	ePoster Session	ePoster Session
15:00-16:00	Sessione plenaria 3 ***La Chimica per la Cultura*** **Prof. Roald HOFFMANN** **PREMIO NOBEL PER LA CHIMICA 1981** Department of Chemistry Cornell University Ithaca USA	**Lavori Divisioni** **12 Sessioni Parallele** **3 (ANA) + 1 (IND) + 4 (ORG) + 1 (CSB) + 1 (DID) + 1 (MAS) + 1 (TEO)**	**Eventi Satellite** **5 Sessioni Parallele** **- Principi attivi e formulazioni in ambito cosmetico** **- Ruolo della Chimica nella produzione e controllo dei farmaci biotecnologici** **- Valorizzazione di scarti di filiere produttive** **- Sostenibilità di polimeri e compositi** **- La conversione e lo stoccaggio dell'energia chimica in energia elettrica, nella vita odierna e nella società futura**	Sessione plenaria 4 ***La Chimica per l'Industria del Futuro*** **Luigi NICOLAIS** Research Policy Advisor to MUR **Avelino CORMA** Institute of Chemical Technology Polytechnical University of Valencia, Spain
16:00-16:30	**Maria Perla COLOMBINI** Dipartimento di Chimica e Chimica Industriale, Università di Pisa			**Lidia ARMELAO** Direttore del Dipartimento di Scienze Chimiche e Tecnologia dei Materiali, CNR
16:30-17:00	Break			Break
17:00-18.00	TAVOLA ROTONDA **Divulgazione scientifica e immagine della Chimica** Partecipano: **Piero Angela** **Silvano Fuso** **Massimo Polidoro** **Luigi Campanella** Coordina: **Giorgio Cevasco**			**Nausicaa ORLANDI** Presidente Federazione Nazionale Ordini Chimici e Fisici **Mario MARCHIONNA** Corporate Head Technology Innovation Saipem
18:00-18:30	Live Q&A Sessione 3	Discussione	Live Q&A	Live Q&A Sessione 4
18:30-19:30	ePoster	e-poster	e-poster	**CONCLUSIONI E CHIUSURA DEL CONGRESSO**

Programma dei LAVORI di DIVISIONE - 15 settembre mattina

Divisione CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI (ABC)
ABC 01

09.30-09.35		**Antonio Marcomini**	*Opening*
09.35-10.00	**ABC IL001**	**Demetrios Anglos**	*Exploring heritage materials and objects via laser spectroscopies*
10.00-10.15	**ABC OR001**	**Gianluigi de Gennaro**	*Sars-CoV-2 airborne transmission: indoor and outdoor implications*
10.15-10.30	**ABC OR002**	**Eleonora Balliana**	*Silk and sanitizing solutions: the need to protect visitor and artworks*
10.30-10.45	**ABC OR003**	**Luca Ciacci**	*Combining the highest degradation efficiency with the lowest environmental impact in zinc oxide based photocatalytic systems*
10.45-11.00	**ABC OR004**	**Cecilia Velino**	*PROCRAFT project: conservation strategies of aircraft heritage from excavation to museum*
11.00-11.30	**break**		
11.30-11.45	**ABC OR005**	**Luca Ferrero**	*Airborne microplastics over the Baltic: influence of sea emissions*
11.45-12.00	**ABC OR006**	**Alessandra Bigogno**	*An indoor air pollution evaluation of the Quarto Stato museum*
12.00-12.15	**ABC OR007**	**Elena Badetti**	*Grafting on metal oxide nanoparticles surface reduces the toxicity of catechols*
12.15-12.30	**ABC OR008**	**Alessandro Ciccola**	*The new shades of the XX century: investigation of ACNA dyes through Raman spectroscopy and HPLC-MS*
12.30-12.45	**ABC OR009**	**Angelo Fenti**	*In Situ Electrochemical Oxidation for Destructive Treatment of PFAS*
12.45-13.00	**ABC OR010**	**Sabina Licen**	*Data fusion techniques based on Self-Organizing Map algorithm for the integration of different source/frequency instrumental data and ancillary information for environmental impact assessment*

Divisione CHIMICA FARMACEUTICA (FAR)
FAR 01

09.30 - 10.00	**FAR KN001**	**Giuseppe Campiani**	*Old but Gold: tracking the new guise of histone deacetylases as biomarkers and therapeutic targets in rare diseases. The role of isoform 6*
10.00 - 10.30	**FAR KN002**	**György M. Keserű**	*The role of the secondary binding pocket in GPCR pharmacology*
10.30 - 10.45	**FAR OR001**	**Agnese Pippione**	*Targeting prostate cancer with multiple-targeting ligands: activity on both AKR1C3 enzyme and androgen receptor*

10.45 - 11.00	**FAR OR002**	**Andrea Spinaci**	*Synthesis and characterization of new A3 adenosine receptors ligands as potential anti-cancer agents*
11.00 - 11.15	**break**		
11.15 - 11.45	**FAR KN003**	**Tracey Pirali**	*The power of multi-component reactions in drug discovery: soft drugs, PROTACs and more*
11.45 - 12.00	**FAR OR005**	**Simona Musella**	*Identification and characterization of a potent TRPM8 antagonists with in vivo analgesic properties*
12.00 -12.15	**FAR OR006**	**Letizia Crocetti**	*Synthesis of pyrazolo[1,5-a]quinazolines as ligand of α1β3γ2-GABAA receptor subtype and molecular modelling studies*
12.15 -12.30	**FAR OR007**	**Carmine Ostacolo**	*Discovery of CP86, a potent neuronal Kv7 channel activator with in vivo anticonvulsant effects*
12.30 - 13.00	**FAR KN004**	**Marco Radi**	*Navigating the antiviral drug discovery space: exploring different routes toward new broad-spectrum agents*

FAR 02

10.30 - 10.45	**FAR OR003**	**Francesca Musumeci**	*Design, synthesis, and biological evaluation of a new series of pyrazolo[3,4-d]pyrimidines active as SGK1 inhibitors. A lead optimization study*
10.45 - 11.00	**FAR OR004**	**Giuseppe La Regina**	*New pyrroles derivatives as anti-glioblastoma and anti-chronic myeloid leukemia agents*
11.00 - 11.45	**break**		
11.45 - 12.00	**FAR OR008**	**Laura Scalvini**	*N-Acylethanolamine acid amidase (NAAA): mechanism of palmitoylethanolamide hydrolysis revealed by mechanistic simulations*
12.00 -12.15	**FAR OR009**	**Leonardo Brunetti**	*Multiple causes, multiple targets: FAAH as a centerpiece for therapy of multifactorial pathologies*
12.15 -12.30	**FAR OR010**	**Rita Turnaturi**	*Influence of the N-substituent of (−)-cis-N-Normetazocine in the modulation of the functional profile at MOR, DOR and KOR: from agonist to antagonist through multitarget ligands*

Divisione CHIMICA FISICA (FIS)

FIS 01

Physical chemistry for Nanomaterials I

09:30-10:00	**FIS KN001**	**Marco Laurati**	*Blunt-end driven assembly of star-like dsDNA coated colloids*
10:00-10:15	**FIS OR001**	**Carlo Nazzareno Dibenedetto**	*Fabrication and spectroscopic investigation of Quantum Dots dimers*
10:15-10.30	**FIS OR002**	**Giovanni LiDestri**	*Forces between nanoparticels at the air/water interface: the role of the ligand chain length*
10:30-10.45	**FIS OR003**	**Davide Peddis**	*Interplay between inter- and intraparticle interactions in bi-magnetic core/shell nanoparticles*
10:45-11:00	**FIS OR004**	**Maryam Abdolrahimi**	*XAS Study of Molecular Coated Manganese Zinc Ferrite Nanoparticles*
11:00-11.15	**FIS OR005**	**Sawssen Slimani**	*Hybrid Spinel Iron Oxide Nanoarchitecture Combining Crystalline and Amorphous Parent Material*
11:15-11.30	**FIS OR006**	**Marco Fabbiani**	*Porous materials for hybrid functional nanocomposites: metal and organic nanowires confined in zeolites and mesoporous silica*
11.30-11.45	**break**		

Physical chemistry for Nanomaterials II

11:45-12:00	**FIS OR007**	**Grazia ML Messina**	*Surfactant vesicles and polysaccharides interactions with cellulose nanocrystals*
12:00_12:15	**FIS OR008**	**Simona Ricci**	*Highly efficient green inkjet printed nanostructured electrodes and SERS substrates*
12:15-12.30	**FIS OR009**	**Marcello Condorelli**	*Ag nanoflowers as single particle SERS active platform*
12:30-12:45	**FIS OR010**	**Valentina Mameli**	*57Fe Mössbauer Spectroscopy and DC magnetometry for the identification of Fe-bearing ultrasmall nanophases in inorganic ordered porous matrixes*
12:45-13:00	**FIS OR011**	**Giovanni Ferraro**	*Controlled decoration of plastic surfaces with metal nanostructures*
13:00-13:15	**FIS OR012**	**Roberta Ruffino**	*“Distorted” self-assembly of polymer thin films at nano-curved surfaces*

FIS 02

PhysicalChemistry for Biomedical Applications I

09:30-10:00	**FIS KN002**	**Paola Sassi**	*Spectroscopic markers of heart failure: a Raman and FTIR study*
10:00-10:15	**FIS OR013**	**Nunzio Tuccitto**	*Quantum Dots Enable Digital Communication Through Biological Fluids*

10:15-10.30	**FIS OR014**	**Elisabetta Fanizza**	*Plasmonic mesoporous silica coated copper sulfide nanoparticles as Near Infrared absorbing photothermal agents*
10:30-10.45	**FIS OR015**	**Rossella Labarile**	*Coating photosynthetic Rhodobacter sphaeroides with polydopamine*
10:45-11:00	**FIS OR016**	**Marco Fornasier (Vincitore del Premio Semerano)**	*A polyphosphoester analog of Pluronic F127 enhances the biocompatibility of monoolein-based cubosomes*
11:00-11.15	**FIS OR017**	**Alberta Terzi**	*X-ray Scattering Scanning Microscopies – novel diagnostic tools of pathologic tissues. A focus on aneurysms, breast cancer and diabetes*
11:15-11.30	**FIS OR018**	**Federica D'Aria**	*G-quadruplex within KRAS gene promoter: a physicochemical study*
11.30-11.45	**break**		

PhysicalChemistry for Biomedical Applications II

11:45-12:00	**FIS OR019**	**Vincenzo De Leo**	*Liposome/Polymer Assembly for Oral Delivery of Curcumin*
12:00_12:15	**FIS OR020**	**Monica Mura**	*Nanoantibiotics: design of multifunctional MSN nanosystems containing both antibiotic and copper ions to combat bone infection*
12:15-12.30	**FIS OR023**	**Elena Piacenza**	*Innovative and green synthesis of biocompatible Selenium nanoparticles in a confined environment with promising antimicrobial activity*
12:30-12:45	**FIS OR024**	**Jennifer Gubitosa**	*Green synthesis of Gold nanoparticles by using grape seeds wastewater: physico-chemical characterization and investigation of their related antioxidant features for cosmetic and biomedical applications*

Divisione CHIMICA INORGANICA (INO)

INO 01

9.30 - 10.30	**INO PZ001**	**Frank Neese**	*Deciphering Inorganic Chemistry Riddles Through a Combination of Spectroscopy and Quantum Chemistry*
10.30 - 10.45	**INO OR001**	**Roberto Gobetto**	*Innovative Mn and Re catalysts for CO2 Photo- and Electro-Reduction*
10.45 - 11.00	**INO OR002**	**Ilaria Barlocco**	*Disclosing the role of Gold on Palladium - Gold alloyed catalysts in formic acid decomposition*
11.00 - 11.15	**INO OR003**	**Cristina Pavan**	*Nearly free silanols on silica surface: a new paradigm for particle toxicology*
11.15-11.30	**break**		

15 settembre - mattina

11.30 - 11.45	**INO OR004**	**Massimo Christian D'Alterio**	*A combined theoretical and experimental investigation of a new class of [N,O-] imidazo[1,5-a]pyrid-3-yl)phenolate Zn(II) catalysts for the ring opening polymerization of lactide*
11.45 - 12.00	**INO OR005**	**Linda Leone**	*Highly selective indole oxidation promoted by a Mn-containing mini-enzyme*
12.00 - 12.15	**INO OR006**	**Javier Martí-Rujas**	*Synthesis and structural properties of isostructural Zn(II) M12L8 poly-[n]-catenane using the 2,4,6-tris(4-pyridyl)benzene (TPB) ligand*
12.15 - 12.30	**INO OR007**	**Francesco Fagnani**	*Three novel families of cyclometalated platinum(II) complexes with remarkable luminescence properties*
12.30 - 13.00	**INO IL001**	**Viktoria Gessner**	*Metallated Ylides: Powerful Reagents for the Stabilization of Reactive Main Group Species and Ligands in Catalysis*

INO 02

10.30 - 10.45	**INO OR008**	**Michele Benedetti**	*"NMR effective molecular radius" of coordinated ammonia*
10.45 - 11.00	**INO OR009**	**Chiara Salvitti**	*Redox reactivity of transition metal dioxide anions towards sulfur dioxide in the gas phase*
11.00 - 11.15	**INO OR010**	**Silvia Ruggieri**	*New chiral heteroleptic Eu(III)/Tb(III)/Yb(III)-based luminescent complexes designed for different applications*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR011**	**Tiziano Marzo**	*Oxaliplatin binds angiogenin and exerts high antiangiogenic effects in PC-3 cancer cells at non-cytotoxic concentration*
11.45 - 12.00	**INO OR012**	**Luca Spitaleri**	*Covalently conjugated gold–porphyrin nanostructures*
12.00 - 12.15	**INO OR013**	**Nicola Panza**	*Ferrate salts as stand-alone catalysts for chemical fixation of CO2 into epoxides and aziridines*
12.15 - 12.30	**INO OR014**	**Elena Lucenti**	*Cyclic triimidazole: an appealing and versatile ligand for the preparation of emissive d9 and d10 metal derivatives*

INO 03

10.30 - 10.45	**INO OR015 premio Wiley**	**Thomas Scattolin**	*Palladium organometallic complexes as promising anticancer agents*
10.45 - 11.00	**INO OR016**	**Caterina Damiano**	*Efficient and low-cost metal-free Porphyrin/TBACl system for the CO2 valorization into N alkyl and N aryl oxazolidin-2-ones*
11.00 - 11.15	**INO OR017**	**Carlo Nervi**	*Transition metal complexes as redox catalysts for CO2 conversion*
11.15-11.30	**break**		

11.30 - 11.45	**INO OR018**	**Cristina Tubaro**	*Gold(I) and gold(III) complexes with thioether- and phosphonium- functionalized N-heterocyclic carbene ligands*
11.45 - 12.00	**INO OR019**	**Marco Baron**	*Manganese(III) complexes with tetradentate O^C^C^O ligands: synthesis, characterization and preliminary catalytic studies on the CO2 cycloaddition with epoxides*
12.00 - 12.15	**INO OR020**	**Roberto Esposito**	*MOF catalyzed ketalization of glycerol into solketal*
12.15 - 12.30	**INO OR021**	**Francesco Ferretti**	*Heterocycles from nitro compounds: CO surrogates in the Pd catalyzed synthesis of carbazoles*

Divisione CHIMICA PER LE TECNOLOGIE (TEC)
TEC 01

09.30 - 10.00	**TEC IL001**	**Alberto Rainer**	*Nanogels as smart drug delivery systems*
10.00 - 10.15	**TEC KN001**	**Claudia Espro**	*Hydrothermal Carbonization as a sustainable approach for the single-step upgrading of industrial citrus processing waste into platform chemicals and biocarbon*
10.15 - 10.30	**TEC KN002**	**Fabrizio Monica**	*Chemistry of materials for energy technologies*
10.30 - 10.40	**TEC OR001**	**Virginia Venezia**	*Biowaste as valuable resource: humic acids valorization into multifunctional materials*
10.40 - 10.50	**TEC OR002**	**Francesco Mauriello**	*Sustainable Valorization of Anchovy Leftovers into Value Added Chemicals, Products and Energy*
10.50 - 11.00	**TEC OR003**	**Carlo Punta**	*Eco-design of Cellulose NanoSponges for water decontamination*
11.00 - 11.10	**TEC OR004**	**Ermelinda Bloise**	*CNSL components as green building-blocks for bio-based nanovesicles*
11.10 - 11.30	**Discussion**		
11.30 - 11.50	**Break**		
11.50 - 12.00	**TEC OR005**	**Manfredi Caruso**	*N-Hydroxyphthalimide role in Aerobic Oxidations: Homogeneous versus Heterogeneous Catalysis*
12.00 - 12.10	**TEC OR006**	**Laura Riva**	*Co-Polymeric Nanosponges from Cellulose Biomass as Heterogeneous Catalysts for Organic Reactions*
12.10 - 12.20	**TEC OR007**	**Serena Regina**	*Use of a bio-derived polymer as crosslinking agent for stable-polyvinyl alcohol membrane development*
12.20 - 12.30	**TEC OR008**	**Simona Sabbatini**	*Thermal-Oxidative Stability of PHBV/LDH Nanocomposites*
12.30 - 12.50	**Discussion**		

12.50 - 13.00	**TEC OR009**	**Angela Marotta**	*Furan as platform molecule in the production of greener epoxy-resins*
13.00 - 13.10	**TEC OR010**	**Franca Castiglione**	*Insights on Ionic Liquids structure and dynamics: NMR methods and recent advances*
13.10 - 13.20	**TEC OR011**	**Giselle de Araujo Lima e Souza**	*Ionic conductivity and thermal characterization of DBU-based protic ionic liquids*
13.20 - 13.30	**TEC OR012**	**Maria Enrica Di Pietro**	*Deep Eutectics: what is inside the solvents for the 21st century?*
13.30 - 13.50	**Discussion**		

TEC 02

10.30 - 10.40	**TEC OR013**	**Giulio Pota**	*Mesoporous Silica Nanoparticles: a powerful platform for biocatalysis*
10.40 - 10.50	**TEC OR014**	**Antonella Satira**	*Tandem Catalytic Upgrading of Limonene and Methyl Levulinate promoted by Pd-based Catalysts*
10.50 - 11.00	**TEC OR015**	**Francesco Parrino**	*Synthesis, characterization, and photocatalytic activity of Eu doped ZnO prepared by supercritical antisolvent precipitation route*
11.00 - 11.10	**TEC OR016**	**Cristina Leonelli**	*Microwave-assisted synthesis and isopropanol extraction in the preparation of TiO2 nanoparticle suspensions*
11.10 - 11.30	**Discussion**		
11.30 - 11.50	**Break**		
11.50 - 12.00	**TEC OR017**	**Aurelio Bifulco**	*Hybrid Strategies for the Improvement of the Flame Retardancy of in-situ Silica-Epoxy Nanocomposites cured with Aliphatic Hardener*
12.00 - 12.10	**TEC OR018**	**Isabella Lancellotti**	*Chemical stabilization in a single step process: geopolymerization of tannery wastewater pollutants*
12.10 - 12.20	**TEC OR019**	**Ambra M. Fiore**	*Hematite nanoparticles as promising catalyst*
12.20 - 12.50	**Discussion**		
12.50 - 13.00	**TEC OR021**	**Vincenzina Barbera**	*Functionalization of graphene related materials with biosourced C-3 and C-6 building blocks. From synthesis to applications*
13.00 - 13.10	**TEC OR022**	**Sabina Alessi**	*Polymer/rubber nanofibrous interleaves for the enhancement of delamination resistance of CFRP laminates*
13.10 - 13.20	**TEC OR023**	**Laura Tripaldi**	*Silica Hairy Nanoparticles in Rubber Nanocomposites*
13.20 - 13.30	**TEC OR024**	**Mariachiara Miceli**	*Titanosilicalite as Nickel Support for Methanation Reaction*
13.30 - 13.50	**Discussion**		

Divisione ELETTROCHIMICA (ELE)

ELE 01

09.30 - 10.00	**ELE_KN01**	**Patrizia Mussini**	*Enantioselective Voltammetry & Chiroptical Spectroscopy: Exploring Intriguing Analogies and Connections*
10.00 - 10.15	**ELE_OR02**	**Elisabetta Petri**	*Electrochemically responsive soft actuators*
10.15 - 10.30	**ELE_OR03**	**Carmelo Lo Vecchio**	*NiFe oxide co-catalyst for an enhanced water splitting in photo-electrochemical cells*
10.30 - 10.45	**ELE_OR04**	**Marco Piccinni**	*Synthesis and water dispersion of nickel-iron layered double hydroxides for energy storage applications*
10.45 - 11.00	**ELE_OR05**	**Daniele Rocco**	*Anodic Dimerization of New Donor-Acceptor Oligothiophenes: Electrochemical and Solvatochromic Behavior*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELE_KN06**	**Peter Fischer**	
11.45 - 12.00	**ELE_OR07**	**Giovanni Crivellaro**	*A complex electrochemistry triggering the operation of Vanadium Redox Flow Batteries*
12.00 - 12.15	**ELE_OR08**	**Giampaolo Lacarbonara**	*A spectroelectrochemical study of copper chloro-complexes for high performance copper redox flow batteries*
12.15 - 12.30	**ELE_OR09**	**Jorge Montero**	*Ferrocene and viologen derivatives as electrolytes for pH neutral aqueous organic redox flow batteries*

ELE 02

09.30 - 10.00	**ELE KN10**	**Giovanni Valenti**	*New Insights Into Electrogenerated Chemiluminescence Mechanism for the Enhancement of Bioanalytical Performance*
10.00 - 10.15	**ELE OR11**	**Sara Bonacchi**	*SpectroElectrochemistry of Metal Nanoclusters:new insights into the origin of the photoluminescence*
10.15 - 10.30	**ELE OR12**	**Marco Mazzucato**	*How Decisive is the Iron Precursor Ligand in Fe-N-C Single-Site Formation and Activity for Oxygen Reduction Reaction?*
10.30 - 10.45	**ELE OR13**	**Mattia Parnigotto**	*Water Loss Predictive Tests in Flooded Lead-Acid Batteries*
10.45 - 11.00	**ELE OR14**	**Mattia Reato**	*Electron Transfers in Films of Atomically Precise Metal Nanoclusters*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELE KN15**	**Alessandro Minguzzi**	*In situ/operando X-ray absorption spectroscopy: a swiss-knife for studying (photo)electrodes*

11.45 - 12.00	**ELE OR16**	**Francesco De Bon**	*Para substituted pyridines ligands forms highly active catalysts for ATRP*
12.00 - 12.15	**ELE OR17**	**Danilo Dini**	*EQCM analysis of the process of electrochemical insertion in regioregular alkyl-susbtituted polyterthiophene during n-doping*
12.15 - 12.30	**ELE OR18**	**Matteo Grattieri**	*Bio-inspired intact bacteria-based biohybrid photoanodes*

ELE 03

09.30 - 10.00	**ELEKN19**	**Marc Koper**	*Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide*
10.00 - 10.15	**ELEOR20**	**Maruccia Elisa**	*Nitrogen-containing ordered mesoporous carbons applied as CO2 adsorbents and anode materials in energy storage devices*
10.15 - 10.30	**ELEOR21**	**Fortunati Alessia**	*Ionic liquids for capture and electrochemical Conversion of CO2*
10.30 - 10.45	**ELEOR22**	**Moro Miriam**	*Carbon Nanostructures decorated with Cerium Oxide as selective electrocatalysts for CO2 reduction*
10.45 - 11.00	**ELEOR23**	**Guzman Hilmar**	*CuZnAl-based oxide catalysts for the electrochemical CO2 conversion*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELEKN24**	**Monica Santamaria**	*Electrochemical surface treatments to improve corrosion resistance of light alloys*
11.45 - 12.00	**ELEOR25**	**Zoli Maddalena**	*Facile and scalable synthesis of Cu2O-SnO2 catalyst for the photoelectrochemical CO2 conversion*
12.00 - 12.15	**ELEOR26**	**Magni Mirko**	*Cathodic Plasma Electrolysis & Recovery of Zinc as Coating*
12.15 - 12.30	**ELEOR27**	**Poli Federico**	*Sustainable strategies to improve MFC power output by green supercapacitors and supercapacitive components*

Divisione TECNOLOGIA FARMACEUTICA (TFA)
TFA 01

09.30 - 10.00	**TFA IL001**	**Elias Fattal**	*Lipid and dendrimer-based nanomedicines for siRNA*
10.00 - 10.30	**TFA IL002**	**Stefano Colloca**	*Set up of large scale production process for GRAd-COV2 vaccine*
10.30 - 10.45	***Discussion***		
10.45 - 11.00	**break**		

15 settembre - mattina

11.00 - 11.15	**TFA OR001**	**Ilaria Arduino**	*Microfluidic preparation and characterization of iRGD-functionalized solid lipid nanoparticles for targeted delivery*
11.15 - 11.30	**TFA OR002**	**Angela Bonaccorso**	*Response Surface Methodology for the optimization of Nanogels Polyelectrolyte Complex intended for Ovalbumin nasal delivery*
11.30 - 11.45	**TFA OR003**	**Ilaria Filippin**	*Cellulase as active excipient in HPMC prolonged-release matrices: a novel approach to zero-order kinetics*
11.45 - 12.00	**TFA OR004**	**Stefania Petralito**	*Remote magneto-mechanical actuation of magnetoliposomes by alternating or pulsed magnetic fields*
12.00 - 12.15	**TFA OR005**	**Emma Piacentini**	*Controlled and tunable polymeric micro/nano particles production using membrane technology*
12.15 - 12.30	**TFA OR006**	**Giovanna Rassu**	*Crocetin as both neuroprotective agent and cross-linker for sericin for obtaining new nasal bioactive nanoparticles*
12.30 - 12.45	**TFA OR007**	**Federica Rinaldi**	*Rifampicin loaded liposomes for Mycobacterium abscessus infection treatement: intracellular uptake and antibacterial activity evaluation*
12.45 - 13.00	**TFA OR008**	**Mattia Tiboni**	*An affordable approach to scalable nanomedicine manufacturing: 3D printed microfluidics*
13.00 - 13.15	**TFA OR009**	**Siyuan Deng**	*Development and Characterization of a Novel Redox-responsive Core-shell Structure Nanohydrogel as Intracellular Delivery System*
13.15-13.30	***Discussion***		

Programma dei LAVORI di DIVISIONE - 15 settembre pomeriggio

Divisione CHIMICA ANALITICA (ANA)
ANA 01

15.00 - 15.10	**ANA PL001**	**Claudio Minero**	*INTRODUZIONE*
15.10 - 15.30	**ANA PZ001**	**Luigia Sabbatini**	*Contaminarsi fa bene alla ricerca*
15.30 - 15.50	**ANA PZ002**	**Luigi Mondello**	*Recent Developments in Mass spectrometry and Cutting Edge Scientific Innovation to Characterize Complex Samples*
15.50 - 16.10	**ANA IL001**	**Susy Piovesana**	*New trends for the enrichment and liquid chromatography-mass spectrometry analysis of peptides with protein post-translational modifications*
16.10 - 16.30	**ANA KN001**	**Flavio A. Franchina**	*The value of multidimensional chromatography coupled to mass spectrometry for the non-targeted metabolite profiling of natural products*
16.30 - 16.45	**ANA OR001**	**Alessia Arena**	*Mineral oil investigation in omega-3 rich lipid supplements by using multidimensional liquid-gas chromatography*
16.45 - 17.00	**ANA OR002**	**Carmela Maria Montone**	*Untargeted characterization and quantitative analysis of underivatized fatty acids in Chlorella vulgaris microalgae*
17.00 - 17.15	**ANA OR003**	**Lorenzo Cucinotta**	*Simultaneous Enantiomeric and Isotopic Ratio evaluation of target terpenes in Cannabis sativa essential oils through Enantio-MDGC-C-IRMS*
17.15 - 17.30	**ANA OR004**	**Gemma De Grazia**	*Evaluation of cryogenic effect for target VOCs isolation by a preparative multidimensional gas chromatographic system*
17.30 - 17.45	**ANA OR005**	**Rosangela Elliani**	*DEVELOPMENT OF A RAPID AND SIMPLE PROTOCOL FOR THE ASSAY OF PARABENS AND BISPHENOLS IN HUMAN SALIVA BY SOLID-PHASE MICROEXTRACTION-GAS CHROMATOGRAPHY-TRIPLE QUADRUPOLE MASS SPECTROMETRY*
17.45 - 18.00	**ANA OR006**	**Antonio Ferracane**	*Simultaneous determination of 88 multi-class pesticide residues in four vegetable matrices using reduced QuEChERS extraction and flow-modulated comprehensive two-dimensional gas chromatography-triple quadrupole mass spectrometry*
18.00 - 18.15	**ANA OR007**	**Micaela Galletta**	*Evaluation of use of hydrogen as carrier gas in flow-modulation comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry*

18.15 - 18.30	**ANA OR008**	**Anna Illiano**	*LC-MRM/MS assay for the quantification of some hormonal proteins in serum and follicular fluid of women undergoing in vitro fertilization*

ANA 02

15.50 - 16.10	**ANA KN002**	**Clemente Bretti**	*Removal of environmentally relevant cations: polymer inclusion membranes (PIMs)*
16.10 - 16.30	**ANA KN003**	**Francesco Pellegrino**	*A New Strategy for Overcoming the Volcano in Water Photosplitting: Controlled Periodic Illumination*
16.30 - 16.45	**ANA OR009**	**Raghav Dogra**	*Preliminary evaluation of Magnetic Nanoparticles for glyphosate contaminated water remediation*
16.45 - 17.00	**ANA OR010**	**Federico Girolametti**	*Evaluation of mercury content in red mullet (Mullus barbatus) muscle from the Adriatic Sea in relation to biological factors and sampling area: risk assessment for human consumption*
17.00 - 17.15	**ANA OR011**	**Marco Minella**	*Experimental evaluation of Fenton oxidation coupled with membrane distillation for produced water treatment: benefits, challenges and effluent toxicity*
17.15 - 17.30	**ANA OR012**	**Donatella Nardiello**	*Nanoconfined liquid phase nanoextraction: an innovative extraction technique for ex-situ and in-situ rapid and quantitative determination of benzene derivatives in seawater*
17.30 - 17.45	**ANA OR013**	**Gabriella Pinto**	*Characterization of polyphenolic compounds in food and industrial wastes*
17.45 - 18.00	**ANA OR014**	**Luca Rivoira**	*Iterative protocols for the extraction and quantitation of microplastics from marine sediments and oysters*
18.00 - 18.15	**ANA OR015**	**Saul Santini**	*Validation of a new method for the simultaneous determination of different classes of PBT chemicals in biota samples*
18.15 - 18.30	**ANA OR016**	**Davide Vivado**	*Study of iron speciation in coastal seawater samples of the Ross Sea (Antarctica) by CLE-AdSV*

ANA 03

15.50 - 16.10	**ANA IL002**	**Erika Scavetta**	*Organic Electrochemical Transistors as low cost chemical sensors*
16.10 - 16.30	**ANA IL003**	**Chiara Zanardi**	*Graphene-based electrodes for the detection of biomarkers in sweat*
16.30 - 16.45	**ANA OR017**	**Andrea Bonini**	*A Label-free impedance biosensing assay based on CRISPR/Cas12a collateral activity for bacterial DNA detection*

16.45 - 17.00	**ANA OR018**	**Tiziano Di Giulio**	*Molecularly imprinted polymers-based impedimetric sensor for metal-ion mediated recognition of a dipeptide*
17.00 - 17.15	**ANA OR019**	**Laura Fabiani**	*Magnetic beads combined with carbon black-based screen-printed electrodes for COVID-19: A reliable and miniaturized electrochemical immunosensor for SARS-CoV-2 detection in saliva*
17.15 - 17.30	**ANA OR020**	**Eleonora Macchia**	*Selective Single-Molecule Detection of clinically relevant biomarkers with an Organic Transistor*
17.30 - 17.45	**ANA OR021**	**Federica Mariani**	*Healthcare monitoring using wearable pH sensors*
17.45 - 18.00	**ANA OR022**	**Vincenzo Mazzaracchio**	*A TiO2 /KuQuinone modified screen-printed photoelectrochemical sensor for NADH detection*
18.00 - 18.15	**ANA OR023**	**Gheorghe Melinte**	*Enhancement of lysozyme detection process by using a gold clusters-based electrochemical aptasensor*
18.15 - 18.30	**ANA OR024**	**Filippo Silveri**	*Redox-active graphene film integrated into a smart device for pesticide biosensing*

Divisione CHIMICA FARMACEUTICA (FAR)
FAR 03

15.00 - 15.45	**FAR MD001**	**Kenneth A. Jacobson**	*Pratesi Medal Lecture - Design and Therapeutic Potential of Adenosine and P2Y Receptor Ligands*
15.45 - 16.00	**FAR PZ001**	**Ciro Milite**	*Modulators of Coactivator-Associated Arginine Methyltransferase 1 (CARM-1): There and Back Again*
16.00 - 16.15	**FAR PZ002**	**Mariateresa Giustiniano**	*Isocyanide Chemistry from the Ground (state) to the Star(s): what's the point for a medicinal chemist?*
16.15 - 17.00	**FAR MD002**	**Antonello Mai**	*Giacomello Medal Lecture - Lecture for the receipt of the "Giordano Giacomello" medal by the Medicinal Chemistry Division of the Italian Chemical Society*
17.00 - 17.15	**break**		
17.15 - 17.30	**FAR OR011**	**Marilia Barreca**	*Inhibition of non-Hodgkin lymphoma cell growth by pyrrolo[1,2]oxazole derivatives*
17.30 - 17.45	**FAR OR012**	**Laura Braconi**	*A new strategy to overcome multidrug resistance (MDR) in cancer cells: P-gp and hCAXII multitarget inhibitors*
17.45 - 18.00	**FAR OR013**	**Daniela Carbone**	*Synthesis and preclinical evaluation of a new generation of 1,2,4-triazine-based PDK modulators: a novel therapeutic approach to halt cancer growth.*

18.00 -18.15	**FAR OR014**	**Arianna Gelain**	*Unraveling the interaction mechanism of a benzothiadiazole-2,2-dioxide derivative with STAT3: towards novel direct inhibitors*

FAR 04

17.15 - 17.30	**FAR OR015**	**Lucia Tamborini**	*Flow-based redox biotransformations for food and pharma applications*
17.30 - 17.45	**FAR OR016**	**Federica Ianni**	*Stability of chlorogenic acid as model system after household microwave treatment*
17.45 - 18.00	**FAR OR017**	**Ilaria Frosi**	*Comparison of different extraction methods to recover bioactive compounds from corn waste (Zea mays L.)*
18.00 -18.15	**FAR OR018**	**Martina Contente**	*Valorization of food wastes and residues through glycosidases*

Divisione CHIMICA INDUSTRIALE (IND)

IND 01

Sessione congiunta con Gruppo Interdivisionale Catalisi

15.00 - 15.30	**IND KN001 Medaglia Piero Pino**	**Nicoletta Ravasio**	*Catalysis and Green Deal*
15,30 - 15,40	**IND OR001**	**Eleonora Aneggi**	*Solvent free selective oxidation of benzyl alcohol over supported Ru catalysts*
15.40 - 15.50	**IND OR002**	**Denise Cavuoto**	*The role of support wettability and acidity in the hydrogenation of γ-valerolactone over Cu/SiO2 catalyst*
15.50 - 16,00	**IND OR003**	**Tommaso Tabanelli**	*Improved Catalytic Transfer Hydrogenation of alkyl levulinates with alcohols over ZrO2 based catalysts*
16.00 - 16.10	**IND OR004**	**Eleonora Vottero**	*Reconstruction phenomena in a Pt/γ-Al2O3 catalyst under hydrogenation conditions*
16.10 - 16.20	**IND OR005**	**Maila Danielis**	*Structural Evolution and Enhanced Steam Deactivation Resistance of PtPd/CeO2 Methane Oxidation Catalysts Prepared by Dry Milling*
16.20 - 16.30	**IND OR006**	**Gabriella Garbarino**	*Effect of promoters on the performances of Ni-Al2O3 catalysts for CO2 hydrogenation*
16.30 - 16.45	**Discussion**		
16.45 - 17.00	**break**		
17.00 - 17.20	**IND KN002**	**Walter Cabri**	*The Twelve Principles of Green Chemistry Translation Guide for Palladium Catalyzed Cross Coupling Reactions for Active Pharmaceutical Ingredients Sustainable Productions"*
17.20 - 17.30	**IND OR007**	**Roberto Sole**	*The alkoxycarbonylation of protected propargyl alcohols*

17.30 - 17.40	**IND OR008**	**Aleksandr Voronov**	*Unexpected O-5-exo-dig Cyclization of Propargyl Ureas to Oxazoline-2-amines Catalyzed by Silver Salts*
17.40 - 17.50	**IND OR009**	**Francesco Taddeo**	*Kinetics of solketal synthesis promoted by Iron(III) complex*
17.50 - 18.00	**IND OR010**	**Vinayak. Botla**	*Palladium/Norbornene-Catalyzed Synthesis of 2-Iodobiaryls*
18.00 - 18.10	**IND OR011**	**Stefano Econdi**	*Heterogeneous catalysts for the liquid-phase degradation of simulants of organophosphorus chemical warfare agents*
18.10 -18.30	**Discussion**		

Divisione CHIMICA ORGANICA (ORG)

ORG 01

15.00 - 15.30	**Benvenuto e premiazione (sessioni unificate)**		
15:30 - 16:00	**ORG PZ001**	**Anna Bernardi**	***Medaglia Adolfo Quilico*** *At the crossroad between Chemistry and Biology: interfering with the sugar code using glycomimetics*
16.00 - 16.15	**ORG OR001**	**Alessandro Ajo**	*Nanocages and capsules for drug and peptides delivery*
16.15 - 16.30	**ORG OR002**	**Silvana Alfei**	*Cationic Copolymers: A Promising Option in the Treatment of Drug Resistance in Neuroblastoma Cells*
16.30 - 16.45	**ORG OR003**	**Davide Audisio**	*Direct Carbon Isotope Exchange of Pharmaceuticals via Reversible Decyanation*
16.45 - 17.00	**ORG OR004**	**Sara Battista**	*Antibacterial and physicochemical properties of quatsomes formulated with L-prolinol-derived surfactants*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR005**	**Roberta Bernini**	*Hydroxytyrosol, much more than an antioxidant*
17.45 - 18.00	**ORG OR006**	**Andrea Calcaterra**	*Diels-Alder type adducts from Morus nigra as potent inhibitors of Micobacterium tuberculosis PtpB*
18.00 - 18.15	**ORG OR007**	**Fabrizio Chiodo**	*Carbohydrate-Mediated "Innate" Considerations in Designing Vaccine-Candidates*
18.15 - 18.30	**ORG OR008**	**Martina Cirillo**	*Selective Integrin Ligands Promote Cell Internalization of the antineoplastic agent Fluorouracil*

ORG 02

16.00 - 16.15	**ORG OR009**	**Mariapina D'Onofrio**	*Chemoselective disulfide-coupling for the semisynthesis of ubiquitinated forms of the Alzheimer's associated protein tau*

16.15 - 16.30	**ORG OR010**	**Maria Giulia Davighi**	*New potential carbonic anhydrase inhibitors based on mono and multivalent sugars and iminosugars*
16.30 - 16.45	**ORG OR011**	**Cristina De Castro**	*N-glycan from Paramecium bursaria Chlorella virus MA-1D: reevaluation*
16.45 - 17.00	**ORG OR012**	**Jenny Desantis**	*Design, synthesis, and evaluation of small molecules Proteolysis Targeting Chimeras (PROTACs) to induce androgen receptor degradation*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR013**	**Cristina Di Carluccio**	*Investigation of the molecular recognition of sialoglycans bound to Siglec-like adhesins of Streptococcus gordonii*
17.45 - 18.00	**ORG OR014**	**Rossella Di Guida**	*Structural characterization of the lipooligosaccharide and capsular polysaccharide from the psychrotrophic bacterium Pseudoalteromonas nigrifaciens Sq02*
18.00 - 18.15	**ORG OR015**	**Maria Funicello**	*Switching the anticancer effect to HIV protease inhibition: new heteroaryl-amidic compounds with a pseudo-symmetric core*
18.15 - 18.30	**ORG OR016**	**Dario Gentili**	*Synthesis of small molecules with potential antiviral acitivity against Sars-CoV-2*

ORG 03

16.00 - 16.15	**ORG OR017**	**Vincenzo Algieri**	*Regioselective Synthesis of 1,3,4,5-Tetrasubstituted Pyrazoles by Eliminative Enaminone-Nitrilimine 1,3-Dipolar Cycloaddition*
16.15 - 16.30	**ORG OR018**	**Michael Andresini**	*Nitrogen transfer to sulfenamides: synthesis of sulfinamidines and unexplored sulfinimidate esters as valuable precursors of protected sulfilimines*
16.30 - 16.45	**ORG OR019**	**Marco Ballarotto**	*Substituted 6H-benzo[c]chromenes: synthetic approach via a Diels-Alder/aromatization sequence and computational investigation*
16.45 - 17.00	**ORG OR020**	**Bruno Mattia Bizzarri**	*Aminomaleonitrile inspired prebiotic chemistry as a novel microwave assisted multicomponent tool for the synthesis of imidazole and purine derivatives with anti-influenza activity*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR021**	**Diego Caprioglio**	*The oxidation of phytocannabinoids: a systematic investigation*
17.45 - 18.00	**ORG OR022**	**Marco Colella**	*Use of flow technology for the development of a sustainable synthesis of azetines and azetidines*
18.00 - 18.15	**ORG OR023**	**Dario Corbisiero**	*Enantioselective Synthesis of Polyfunctionalized Isoxazoline Rings: Development of a Methodology for the preparation of Tumor-Oriented Small Molecules*

18.15 - 18.30	**ORG OR024**	**Massimiliano Cordaro**	*Synthetic Approaches to Molecular Diversity of BODIPY*

ORG 04

16.00 - 16.15	**ORG OR025**	**Vincenzo Mirco Abbinante**	*Highly-fluorinated aromatic diimides for organic electronics:from synthesis to thin-film preparation*
16.15 - 16.30	**ORG OR026**	**Rita Argenziano**	*Functional films from 5,6-dihydroxyindole oligomers and long chain diamines partnership*
16.30 - 16.45	**ORG OR027**	**Giacomo Biagiotti**	*Tailoring the structure of the BODIPY probe in the design of functional fluorescent materials*
16.45 - 17.00	**ORG OR028**	**Davide Blasi**	*Trityl-brominated radicals as building blocks for doublet CPL emitters*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR029**	**Alberto Bossi**	*Porphycenes, a lesser known tetrapyrrolic macrocycle with intriguing properties suitable for in situ sensing*
17.45 - 18.00	**ORG OR030**	**Adriano Parodi**	*Polyhydroxybutyrate as a sustainable platform for the production of chemicals and bio-polymers*
18.00 - 18.15	**ORG OR031**	**Simone Di Noja**	*Transfer of Axial Chirality to the Nanoscale Endows Carbon Dots with Circularly Polarized Luminescence*
18.15 - 18.30	**ORG OR032**	**Claudio Ferdeghini**	*Synthesis and thermal behavior of dicationic ionic liquids*

Divisione CHIMICA DEI SISTEMI BIOLOGICI (CSB)

CSB 01

15.00 - 15.05	**Opening Remarks Presidente Michael Assfalg**		
15.05 - 15.35	**CSB KN001**	**Rommie Amaro**	*Computational Microscopy of SARS-CoV-2*
15.35 - 16.00	**CSB PZ001**	**Luca Mazzei**	*Talking about urease: How the grasp on the molecular aspects of this enzyme can help in counteracting its role in microbiological pathogenesis and environmental issues*
16.00 - 16.15	**CSB OR001**	**Marta De Zotti**	*A pH-Induced Reversible Conformational Switch able to control the Photocurrent Efficiency in a Peptide Supramolecular System*
16.15 - 16.30	**CSB OR002**	**Ottavia Bellotto**	*Supramolecular hydrogels from unprotected dipeptides: a comparative study on stereoisomers and structural isomers the Photocurrent Efficiency in a Peptide Supramolecular System*
16.30 - 17.00	**Break**		
17.00 - 17.30	**CSB PZ002**	**Claudia Bonfio**	*Uncovering the emergence of modern cells*
17.30 - 17.45	**CSB OR003**	**Gianantonio Battistuzzi**	*Molecular basis of myoglobinopathy, a newly discovered molecular disease*
17.45 - 18.00	**CSB OR004**	**Lidietta Giorno**	*Selectivity and stability of biological macromolecules heterogenized to nanostructured artificial membranes*

18.00 - 18.15	**CSB OR005**	**Claudia Riccardi**	*Design, synthesis and characterization of cyclic TBA analogues*
18.15 - 18.50	**Discussione**		

Divisione DIDATTICA CHIMICA (DID)
DID 01

15:00-16:00	**DID PL001**	**Jan Apotheker**	*Developments in chemistry education*
16:00-16:30	**DID IL001**	**Mariano Venanzi**	*Sustainable chemistry for a sustainable teaching. A proposal for a first level curriculum in Chemistry at University*
16:30-16:45	**DID OR001**	**Federica Branchini**	*Teaching the notion of chemical bonding: a didactic challenge*
16:45-17:00	**DID OR002**	**Maria Antonietta Carpentieri**	*A new didactic pathway to introduce Spectroscopy by historical-epistemiological/STEM laboratorial/distance learning blended approach*
17:00-17:15	**DID OR003**	**Maria Costa**	*Virtual Reality visualizations of complex molecular structures in chemistry education. The β-CD-ASA example*
17:15-17:30	**DID OR004**	**Sandro Jurinovich**	*A didactic sequence for teaching chromatography: observation, model and practical applications*
17:30-17:45	**DID OR005**	**Dora Stella Lombardi**	*'Light and Molecules': an experimental approach to the understanding of basic concepts of Quantum Mechanics*
17:45-18:00	**DID OR006**	**Alma Moretta**	*Additional Learning Requirements (OFA) in Math for Environmental Science degree course: a review for a better understanding of the difficulties of students entering university*
18:00-18:15	**DID OR007**	**Davide Peddis**	*From the astro to the nano scale: a learning by doing teaching pathway*
18:15-18:30	**DID OR008**	**Antonio Testoni**	*Chemistry, history and complexity*
18:30-18:45	**DID OR009**	**Sergio Palazzi**	*A colorful new morning - teaching applied chemistry in pandemic times*

Divisione SPETTROMETRIA DI MASSA (MAS)
MAS 01

15.00 - 15.15	**Welcome**		
15.15 - 15.55	**MAS PL001**	**Giuseppina Maccarone**	*The Role of Mass Spectrometry in the – omics Era*
15.55 - 16.10	**MAS OR001**	**Daniela Cecconi**	*Integrated lipidomics and proteomics reveal cardiolipin remodelling, upregulation of HADHA and long chain fatty acids in pancreatic cancer stem cells*
16.10 - 16.25	**MAS OR002**	**Silvia Pedretti**	*Metabolomic approaches to investigate the role of the mitochondrial*
16.25 - 16.35	**Break**		

16.35 - 17.15	**MAS PL002**	**John A. McLean**	*High dimensional molecular phenomics in systems, synthetic, and chemical biology*
17.15 - 17.30	**MAS OR003**	**Isabella Piga**	*Spatial proteomics to map tissue alterations during the progression of fibrosis in an IPF and Nintedanib-treated mouse model*
17.30 - 17.45	**MAS OR004**	**Federico Fanti**	*Quantitative analysis of resolvins in biological matrices by means LLE-μSPE-HPLC-MS/MS*
17.45 - 18.00	**MAS OR005**	**Elettra Barberis**	*A Combined GCxGC-MS and GC-MS Approach to Discovery and Validate New Potential Biomarkers for Prostate Cancer Diagnosis*

Divisione TEORICA E COMPUTAZIONALE (TEO)

15:00 -15:20	**TEO KN001**	**Emilia Sicilia**	*Computations for investigating anticancer activity of metal-based compounds beyond cisplatin*
15:20 - 15:40	**TEO PZ001**	**Greta Donati**	*Exploring Chemistry through Multiple Time and Size Scales*
15:40 - 15:50	**TEO OR001**	**Marco Bertani**	*Improving empirical force fields for molecular dynamics simulations of oxide glasses. The importance of three-body interactions in rigid-ion models*
15:50 - 16:00	**TEO OR002**	**Arianna Massaro**	*First-principles study of Oxygen redox activity in P2-type NaxNi0.25Mn0.68O2 high energy cathode for Na-ion batteries*
16:00 - 16:10	**TEO OR003**	**Mirko Vanzan**	*An atomistic insight on the hot-electron injection mechanism*
16:10 - 16:20	**TEO OR004**	**Sergio Tosoni**	*Computational characterization of single-atom species on metal-supported oxide thin films*
16:20 - 16:30	**TEO OR005**	**Ida Ritacco**	*Spontaneous Production of Ultrastable Reactive Oxygen Species on Titanium Oxide Surfaces Modified with Organic Ligands*
16:30 - 17:00	**break**		
17:00 - 17:20	**TEO PZ002**	**Alessandro Erba**	*The Role of Fock Exchange in Relativistic Density Functional Theory*
17:20 - 17:30	**TEO OR006**	**Luca Brugnoli**	*Development and application of a ReaxFF Reactive Force Field for Cerium Oxide/Water Interfaces*
17:30 - 17:40	**TEO PO005**	**Anna Ranaudo**	*Computational study on the structural stability of mutated Affitins*
17:40 - 17:50	**TEO OR008**	**Noelia Faginas-Lago**	*Molecular Simulations of CO2/N2/H2O Gaseous Mixture Separation in Graphtriyne Membrane*
17:50 - 18:00	**TEO OR009**	**Francesca Fasulo**	*Electrode-electrolyte interface in solid-state lithium batteries: new insights from density functional embedding theory*

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18:00 - 18:10	**TEO OR010**	**Mariagrazia Fortino**	*Multi-replica biased sampling for photoswitchable p-conjugated polymers*
18:10 - 18:30	**discussion**		

Programma dei LAVORI di DIVISIONE - 16 settembre mattina

Divisione CHIMICA ANALITICA (ANA)

ANA 04

09.30 - 09.50	**ANA IL004**	**Cosima Damiana Calvano**	*Allergenicity assessment of novel foods by identifying marker peptides using bioinformatics and LC-ESI-MS/MS*
09.50 - 10.10	**ANA OR024**	**Danilo Corradini**	*Separation and Detection of Charged and Neutral Biomolecules in Plants and Food Matrices by Capillary Zone Electrophoresis*
10.10 - 10.15	**break**		
10.15 - 10.30	**ANA OR025**	**Antonella Cavazza**	*Analytical approaches for safety assessment in the development of innovative packaging solutions*
10.30 - 10.45	**ANA OR026**	**Tatiana Chenet**	*Evaluation of the presence of plastics in two fish species of the Mediterranean Sea and potentially correlated harmful effects*
10.45 - 11.00	**ANA OR027**	**Paola Arena**	*A Holistic Approach to the Characterization of High-Value Generating Molecules from the Wastes of Tuna Fishery Industry*
11.00 - 11.15	**ANA OR028**	**Federica Dal Bello**	*Insects food for the future*
11.15 - 11.30	**ANA OR029**	**Debora fabbri**	*Integrated approach for the analysis of some pesticides in vegetables and food matrices fastidiosa*
11.30 - 11.45	**ANA OR030**	**Paola Agata E. Donato**	*Triacylglycerol Fingerprinting in Vegetable Oils by means of Subcritical Solvent Chromatography*
11.45 - 12.00	**ANA OR031**	**Marco Iammarino**	*Exploring the potentiality of capillary ion chromatography (CIC) as analytical technique for the determination of food additives*
12.00 - 12.15	**ANA OR032**	**Fabio Salafia**	*Use of ultra-high performance liquid chromatography to characterize non-volatile compounds in Italian beers*
12.15 - 12.30	**ANA OR033**	**Emanuela Trovato**	*Characterization of volatile and non volatile compounds in citrus beer to evaluate product quality for food frauds prevention.*

ANA 05

09.30 - 09.50	**ANA KN004**	**Alessandra Biancolillo**	*Variable selection with a focus on multi-way and multi-block data*
09.50 - 10.10	**ANA KN005**	**Cristina Malegori**	*Near infrared hyperspectral imaging combined with multivariate image analysis: potential and limitations for the identification of microplastics in aquatic samples*
10.10 - 10.15	**break**		
10.15 - 10.30	**ANA OR034**	**Giacomo Baccolo**	*Automate chemometric approach for peak identification and quantification in untargeted GC-MS data*

10.30 - 10.45	**ANA OR035**	**Denise Biagini**	*Oxylipin storm in COVID-19: a new perspective in classifying disease severity*
10.45 - 11.00	**ANA OR036**	**Francesca Di Donato**	*Authentication of donkey's milk by Near Infrared Spectroscopy coupled with chemometric classifiers*
11.00 - 11.15	**ANA OR037**	**Fabio Fornari**	*Connecting the dots between theory and practice: discovering new functional cocrystals through supervised pattern recognition*
11.15 - 11.30	**ANA OR038**	**Sabina Licen**	*SOMEnv: an R package for mining environmental monitoring datasets by Self-Organizing Map and k-means algorithms with a Graphical User Interface*
11.30 - 11.45	**ANA OR039**	**Lisa Rita Magnaghi**	*Optode & Chemometrics: Milk Freshness at a Glance*
11.45 - 12.00	**ANA OR040**	**Elisa Robotti**	*Optimization of the process of anaerobic digestion of FORSU by experimental design techniques*
12.00 - 12.15	**ANA OR041**	**Giorgia Sciutto**	*A chemometric strategy to exploit the complementary information from a combined XRF-Vis-NIR hyperspectral imaging system*
12.15 - 12.30	**ANA OR042**	**Federica Turrini**	*'Specialty' or 'Gourmet' oils: a multivariate statistical approach for the rapid identification of their botanical species*

ANA 06

09.30 - 09.50	**ANA KN006**	**Serena Arnaboldi**	*Unconventional Electrochemical Approaches for the Direct Readout of Chiral Information*
09.50 - 10.10	**ANA KN007**	**Isacco Gualandi**	*Electrosynthesis of Layered Double Hydroxides for analytical applications*
10.10 - 10.15	**break**		
10.15 - 10.30	**ANA OR043**	**Riccarda Antiochia**	*Wearable electrochemical microneedles-based nanoporous gold sensor for real time catecholamine detection*
10.30 - 10.45	**ANA OR044**	**Paolo Inaudi**	*Solid state electrochemical behaviour and spin multiplicity in charge transfer co-crystals of DBTTF:F4TCNQ*
10.45 - 11.00	**ANA OR045**	**Andreas Lesch**	*Large-scale production of electroanalytical sensors by combined inkjet printing and light-induced synthesis of metal nanoparticles*
11.00 - 11.15	**ANA OR046**	**Antonella Miglione**	*Combined paper-based substrates for electrochemical detection of copper ions in serum*
11.15 - 11.30	**ANA OR047**	**Patrizia R. Mussini**	*Enantiomer discrimination in voltammetry in media of high structural order at the electrochemical interphase implemented with chirality*

11.30 - 11.45	**ANA OR048**	**Laura Pigani**	*Cannabinoids fast detection in real matrices: an electrochemical sensors' approach*
11.45 - 12.00	**ANA OR049**	**Angelo Tricase**	*Electrochemical Characterization of supramolecular structure in Self-Assembled Monolayers*
12.00 - 12.15	**ANA OR050**	**Martina Vizza**	*Specific ion effect in electrochemistry: the deposition of copper in the presence of different background electrolytes*

Divisione CHIMICA FISICA (FIS)

FIS 03

Enerchem I

09:30-10:00	**FIS KN003**	**Emanuela Gatto**	*Photocurrent Generation in Supramolecular Bio-Inspired Nanoarchitectures on Gold Surface*
10:00-10:15	**FIS OR025**	**Cristina Artini**	*A novel approach for the evaluation of the defect clusters content in doped ceria through in-situ high pressure x-ray diffraction*
10:15-10.30	**FIS OR026**	**Chiara Milanese**	*Super activated biochar for solid state hydrogen storage and supercapacitors preparation*
10:30-10.45	**FIS OR027**	**Emanuela Sartori**	*Emissive Layered Perovskite Nanocrystals*
10:45-11:00	**FIS OR028**	**Giovanni Di Liberto**	*Theoretical Description Semiconductors Interfaces: insights from DFT*
11:00-11.15	**break**		

Enerchem II

11:15-11.30	**FIS OR029**	**Vanira Trifiletti**	*Synthesis of bismuth-based hybrid perovskites for thermoelectrics*
11.30-11.45	**FIS OR033**	**Mariarosaria Tuccillo**	*Operando study of a cobalt free Li-rich layered oxide materials (LRLO) in a lithium cell*
11:45-12:00	**FIS OR031**	**Simone Sansoni**	*Laser ablation in solution for a more sustainable perovskite-based optoelectronics*
12:00-12:15	**FIS OR030**	**GianLuca Chiarello**	*Photothermocatalytic steam reforming of methanol for H2 production*
12:15-12.30	**FIS OR032**	**Annalisa Polo (Vincitrice del Premio Semerano)**	*Effects of Mo6+ doping on the performance of BiVO4 photoanodes for solar water oxidation*

FIS 04

Physical Chemistry for Environment I

09:30-10:00	**FIS KN004**	**Luigi Gentile**	*Ecofriendly Isolation of Cellulose from buckwheat chaff*
10:00-10:15	**FIS OR039**	**Vito Rizzi**	*From agricultural wastes to a resource: Kiwi Peels as recyclable adsorbent to remove emerging pollutants from water*

10:15-10.30	**FIS OR035**	**Giuseppina Anna Corrente**	*Hydrochemical study of the Turbolo basin: evaluation of the spatial and seasonal variation of surface water quality*
10:30-10.45	**FIS OR036**	**Vanessa Miglio**	*Silica Monolith for the Removal of Pollutants from Gas and Aqueous Phases*
10:45-11:00	**FIS OR037**	**Gabriele Mulas**	*Investigation of mechanochemically driven CO2 conversion over Olivine powders*
11:00-11.15	**break**		

Physical Chemistry for Environment II

11:15-11.30	**FIS OR038**	**Pier Luigi Gentili**	*Establishing a link between Chemistry and Complexity Science to promote Sustainability*
11.30-11.45	**FIS OR034**	**Sebastiano Campisi**	*Tin-functionalized hydroxyapatite as an "ecofriendly bridge" joining water remediation and air protection processes*
11:45-12:00	**FIS OR040**	**Paolino Caputo**	*Use of Food Substances as chemical additives in the industrial field*
12:00_12:15	**FIS OR041**	**Alessio Zuliani**	*Environmentally friendly ZnO/Castor oil polyurethane composites for the efficient gas-phase adsorption of acetic acid*
12:15-12.30	**FIS OR042**	**Antonio Tursi**	*Synthesis and Enhanced Capture Properties of a New BioMOF@SWCNT-BP: Recovery of the Endangered Rare Earth-Elements from Aqueous Systems*

FIS 05

Spectroscopic Applications I

09:30-10:00	**FIS KN005**	**Elena Groppo**	*Revisiting the use of probe molecules in the characterization of heterogeneous olefin polymerization catalysts by IR spectroscopy*
10:00-10:15	**FIS OR043**	**Giampaolo Marcolin**	*Solvent-dependent Characterization of Fucoxanthin through 2D Electronic Spectroscopy Reveals New Details on the Intramolecular Charge Transfer State Dynamics*
10:15-10.30	**FIS OR044**	**Alessandra Forni**	*Multiple prompt and long-lived emissions from solid state purely organic materials*
10:30-10.45	**FIS OR045**	**Rosachiara Antonia Salvino**	*NMR in chiral partially ordered media: a tool for achieving conformational traits of small flexible enantiomers in solution*
10:45-11:00	**FIS OR046**	**Nicola Peruffo**	*Selective Switching of Multiple Plexcitons in Colloidal Materials: Directing the Energy Flow at the Nanoscale*

Spectroscopic Applications II

11:15-11.30	**FIS OR047**	**Elisabetta Collini**	*The effect of hydrogen bonds on the ultrafast relaxation dynamics of a BODIPY dimer*
11.30-11.45	**FIS OR048**	**Francesca Martini**	*Structure and dynamics of "cool" organic pigments by solid state NMR*

11:45-12:00	**FIS OR049**	**Margherita Bolognesi**	*Bidimensional black Phosphorus: surface functionalization, heterostructures with organic molecules, applications*
12:00_12:15	**FIS OR050**	**Annamaria Panniello**	*BODIPY-functionalized Quantum dots platform for high efficiency FRET processes*
12:30-12:45	**FIS OR093**	**Eleonora Vottero**	*C-H terminations in activated carbons and related catalysts:an Inelastic Neutron Scattering spectroscopy and DFT study*

Divisione CHIMICA INDUSTRIALE (IND)
IND 02

Sessione congiunta con Gruppo Interdivisionale Catalisi

09.30 - 9.40	**IND OR012**	**Annalisa Sacchetti**	*Bio-oils valorization by selective catalytic hydrogenation: a comparison between batch and continuous flow systems*
9.40 - 9.50	**IND OR013**	**Alessandra Toso**	*Pd/CeO2 as Passive NOx Adsorbers: key properties and NOx adsorption mechanism*
9.50 - 10.00	**IND OR014**	**Sebastiano Campisi**	*A green route to the catalytic nitrous oxide decomposition by transition metal doped hydroxyapatites*
10.00 - 10.10	**IND OR015**	**Luca Consentino**	*Ce doped WO3-TiO2 cordierite monoliths for Selective Catalytic Reduction of NOx by NH3*
10.10 - 10.20	**IND OR016**	**Roberto Fiorenza**	*The solar photothermo-catalytic approach for the VOCs degradation and the subsequent CO2 conversion*
10.20 - 10.30	**IND OR017**	**Melissa Greta Galloni**	*Cu, Fe, and CuFe exchanged hydroxyapatites as eco-friendly catalysts for NH3-SCR reaction*
10.30 - 10.45	**Discussion**		
10.45 - 11.00	**break**		
11.00 - 11.20	**IND KN003**	**Pierdomenico Biasi**	*From University to Industry: examples on how university-industry collaborations in catalysis can be effective and successful*
11.20 - 11.30	**IND OR018**	**Fabiana Vento**	*Photodegradation of Xenobiotics from Polluted Water Using a New PMMA-TiO2 Based Nanocomposite*
11.30 - 11.40	**IND OR019**	**Vincenzo Russo**	*Heterogeneous photodegradation for the removal of ibuprofen from water*
11.40 - 11.50	**IND OR020**	**Alessandro Allegri**	*Aquivion® PFSA-based spray-freeze dried composite materials for the conversion of furfuryl alcohol to levulinates*
11.50 - 12.00	**IND OR021**	**Somayeh Taghavi**	*Biomass-derived levulinic acid hydrogenation to GVL using bifunctional biochar-based catalysts*
12.00 - 12.10	**IND OR044**	**Giulia Zoppi**	*Green hydrogen production from wastewater derived from lignin-rich hydrothermal liquefaction*
12.10 - 12.30	**Discussion**		

IND 03

09.30 - 9.50	**IND KN004**	**Michele Laus**	*Polymer brush technology: the true and the false in grafting to processes*
9.50 - 10.00	**IND OR023**	**Stefano Gazzotti**	*1,3-Dioxolan-4-Ones as powerful tool for the synthesis of functionalized PLA-based materials with tailored properties*
10.00 - 10.10	**IND OR024**	**Carla Calabrese**	*Hybrid organic-inorganic materials based on polydopamine-like chemistry*
10.10 - 10.20	**IND OR025**	**Alessandro Piovano**	*ß-ketoimine Cr complexes for the production of functional polyolefins: exploring the metal-ligand bond as a key point of the catalysts*
10.20 - 10.30	**IND OR026**	**Edoardo Podda**	*Self-Healing and Shape-Memory Hydrogels by Micellar Polymerization*
10.30 - 10.40	**IND OR027**	**Riccardo Chiarcos**	*Evidence of Preferential Grafting of Short Chains in Grafting To Reactions of Hydroxy-Terminated P(S-r-MMA) Copolymers*
10.40 - 10.55	**Discussion**		
10.55 - 11.10	**break**		
11.10 - 11.20	**IND OR028**	**Antonietta Cozzolino**	*Axially oriented guest induced crystallization in syndiotactic polystyrene unstretched fiber*
11.20 - 11.30	**IND OR029**	**Manohar Golla**	*Axially Oriented Co-crystalline Phases of Poly(2,6-dimethyl-1,4-phenylene)oxide and host-guest orientations*
11.30 - 11.40	**IND OR030**	**Camilla Parmeggiani**	*Liquid crystal elastomer based artificial muscles for cardiac repair*
11.40 - 11.50	**IND OR031**	**Daniele Martella**	*Cell instructive polymers based on liquid crystals*
11.50 - 12.00	**IND OR032**	**Nicole Mariotti**	*Bio-based and waste-derived polyurethanes for energy systems*
12.00 - 12.30	**Discussion**		

Divisione CHIMICA ORGANICA (ORG)

ORG 05

10.00 - 10.30	**ORG PZ005**	**Marco Lucarini**	***Premio alla ricerca Chimica Organica nei suoi Aspetti Metodologici*** *Novel Spin-Labelled Mechanically Interlocked Molecules as Models for the Interpretation of Biradical EPR Spectra*
10.30 - 10.45	**ORG OR033**	**Fabio Buonsenso**	*Non-equilibrium dynamic chromatography: investigation of the reduction process of α-lipoic acid promoted by dithiothreitol*
10.45 - 11.00	**ORG OR034**	**Marta Da Pian**	*Combined use of forensic science in sexual assault: a case report*

11.00 - 11.15	**ORG OR035**	**Graziano Di Carmine**	*Aldol Reaction between Benzaldehyde and Hydroxyacetone Promoted by Silica SBA-15 supported proline: Unraveling the Solvent Effect on the Catalyst Behavior Using NMR Relaxation*
11.15 - 11.30	**ORG OR036**	**Elena Ermini**	*New 1-6 self-immolative spacer for the release of thiols under nitroreductase activation*

ORG 06

10.30 - 10.45	**ORG OR037**	**Germana Esposito**	*Molecular Networking: a powerful tool to dereplication of natural products*
10.45 - 11.00	**ORG OR038**	**Roberta Franzini**	*Chromatographic and spectroscopic investigation of chiral aza-dibenzocyclooctynes and their analogues obtained by azido-click reaction.*
11.00 - 11.15	**ORG OR039**	**Marco Galeotti**	*Hydrogen Atom Transfer based aliphatic C-H bond oxidation of hydrocarbons bearing cyclopropyl moieties. The role of hyperconjugation.*
11.15 - 11.30	**ORG OR040**	**Chiara Lambruschini**	*Photoisomerization of ferulic acid derivatives*

ORG 07

10.30 - 10.45	**ORG OR041**	**Francesca Ghirga**	*Development of ArnT-mediated colistin resistance diterpene-based inhibitors*
10.45 - 11.00	**ORG OR042**	**Laura Goracci**	*Exploring PROTACs metabolism: a structure-activity relationship study*
11.00 - 11.15	**ORG OR043**	**Concetta Imperatore**	*Toward marine inspired multitarget drugs for diabetes mellitus and its complications: design and synthesis of novel dual Protein Tyrosine Phosphatase 1B and Aldose Reductase ligands*
11.15 - 11.30	**ORG OR044**	**Marco Masi**	*Phytotoxins produced by fungal pathogens of legume crops*

Divisione CHIMICA DEI SISTEMI BIOLOGICI (CSB)

CSB 02

09.30 - 10.00	**CSB KN002**	**Paola Turano**	*Bioinorganic chemistry of ferritin nanocages*
10.00 - 10.15	**CSB OR006**	**Veronica Ghini**	*NMR as a tool to monitor the individual response of immunotherapy*
10.15 - 10.30	**CSB OR007**	**Luigi Russo**	*μs-ms conformational dynamics control the formation of prion protein intermediate states involved in amyloid fibrils*
10.30 - 10.45	**CSB OR008**	**Sabrina Elkhanoufi**	*New, highly sensitive off/on EPR probes to monitor enzymatic activity*
10.45 - 11.00	**CSB OR009**	**Alessia Distefano**	*A MS and SPR coupled approach to fully characterize IDE activity modulation*

11.00 - 11.15	**Break**		
11.15 - 11.30	**CSB OR010**	**Alessandro D'Urso**	*The increased thermodynamic stability of miRNAs might be the reason of stronger repressive activity*
11.30 - 11.45	**CSB OR029**	**Anna Di Porzio**	*Identification of a short peptide that preferentially binds to the G-quadruplex structure in the c-MYC oncogene promoter*
11.45 - 12.00	**CSB OR012**	**Chiara Platella**	*Targeting cancer-related DNA G-quadruplex structures by naphthalene diimide ligands*
12.00 - 12.15	**CSB OR013**	**Alessandra Romanelli**	*Self-assembly of PNA-peptide conjugates*
12.15 - 12.45	**Discussione**		

Divisione ELETTROCHIMICA (ELE)
ELE 04

09.30 - 10.00	**ELE IL28**	**Sara Rebeccani**	*PEDOT doped with Sulphonated Polyarylethersulphones as electroactive material in electroanalytical applications*
10.00 - 10.15	**ELE IL29**	**Cecilia Wetzl**	*Graphene-based functional materials for electrochemical imaging*
10.15 - 10.30	**ELE IL30**	**Lorenzo Ripani**	*Microkinetic modeling for the electrochemical CO2 reduction reaction in bicarbonate electrolyte*
10.30 - 10.45	**break**		
10.45 - 11.00	**ELE IL31**	**Riccardo Brandiele**	*Synthesis and characterization of materials for PEM-FC, based on Pt alloyed nanoparticles supported on next generation mesoporous carbon*
11.00 - 11.15	**ELE IL32**	**Annalisa Polo**	*Ternary Oxide Semiconductor Photoanodes for Solar Energy Conversion*
11.15 - 11.45	**ELE IL33**	**Laura Rotundo**	*Electroreduction of carbon dioxide by Re(I) and Mn(I) bipyridine complexes*

Divisione CHIMICA PER LE TECNOLOGIE (TEC)
TEC 03

9.30 - 9.40	**TEC OR025**	**Paola Di Matteo**	*Phenolic compounds in alcoholic and low-alcoholic beer by fast HPLC-PDA-MS/MS analysis: impact of malt composition, hops and dealcoholization process.*
9.40 - 9.50	**TEC OR026**	**Elhussein M. F. M. H. Ahmed**	*Early-Detection of Xylella fastidiosa in Olive Trees by Hyperspectral Reflectance and Non-targeted Metabolomics*
9.50 - 10.00	**TEC OR027**	**Nazeeha Ayaz**	*Hydrophobin coated superfluorinated nanoparticles for 19F-MRI cell tracking*
10.00 - 10.10	**TEC OR028**	**Elena Dilonardo**	*S-PEEK membranes optimized for Vanadium Redox Flow Battery: the effects of sulphonation degree and filler content on operative conditions and set-up configurations*

10.10 - 10.20	**TEC OR029**	**Giuseppe Marcì**	*Selective photocatalytic partial oxidation of aromatic alcohols to aldehydes in aqueous suspensions of C3N4 obtained by polycondensation of melamine and cyanuric/barbituric acids*
10.20 - 10.40	**Discussion**		
10.40 - 10.50	**TEC OR030**	**Giancarlo Terraneo**	*Crystalline Molecular Rotors Assembled through Halogen Bonding*
10.50 - 11.00	**TEC OR031**	**Valentina Dichiarante**	*Multi-branched perfluoro-tert-butoxyl scaffolds for the functionalization of surfaces and nanomaterials*
11.00 - 11.10	**TEC OR032**	**Gabriella Munzi**	*A dinuclear Zn(II) Schiff-base complex as molecular tweezer: binding properties and sensing towards biogenic diamines*
11.10 - 11.20	**TEC OR033**	**Martina Lippi**	*Dynamic 1D Bispidine-based Coordination Polymers for Adsorption Applications*
11.20 - 11.30	**TEC OR034**	**Daniele Narzi**	*Mechanism of oxygen evolution and Mn4Ca cluster restoration in the natural water-oxidizing catalyst*
11.30 - 11.50	**Discussion**		

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Divisione CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI (ABC)

ABC 02

09.30-10.00	**ABC KN001**	**Edith Joseph**	*Green methods for metals conservation*
10.00-10.15	**ABC OR023**	**Francesco Abate**	*The evolving perspective on the study of ancient bronze coins*
10.15-10.30	**ABC OR024**	**Cecilia Velino**	*Investigation of the corrosive effects of ambient particulate matter on bronze through accelerated sampling and ageing*
10.30-10.45	**ABC OR025**	**Maria Labate**	*The leading role of diagnostics for cultural heritage in historic studies and conservation: Sarezzano reliquary busts as a case study*
10.45-11.00	**ABC OR026**	**Andrea Timoncini**	*Characterization of bacteria community on bronze and marble statues*
11.00-11.15			
11.15-11.30			
11.30-11.45	**ABC OR027**	**Roberta Zanini**	*Laser Ablation ICP-MS elemental imaging to investigate corroded surfaces of ancient glass*
11.45-12.00	**ABC OR028**	**Lucrezia Gatti**	*A new analytical strategy for the characterization of diagenetic pathways in ancient bones and teeth.*
12.00-12.15	**ABC OR029**	**Raffaella Lamuraglia**	*Archaeometric investigation on Roman frescoes from the archaeological site of Aquileia*
12.15-12.30	**ABC OR030**	**Francesca Porpora**	*Diammonium hydrogen phosphate and Ca (OH)2 nanoparticles for consolidation of ancient bones: evaluation of performances*
12.30-12.45	**ABC OR052**	**Serena Spadavecchia**	*Evaluation of the effectiveness of coatings for the protection of outdoor terracotta artworks through artificial ageing*
12.45-13.00	**ABC OR032**	**Giulia C. Lodi**	*The assessment of the organic composition of historical remedies and drugs through a multidisciplinary approach*

ABC 03

09.30-09.45	**ABC OR034**	**Antonino Fiorentino**	*New photo-Fenton like process for roof harvested rainwater disinfection*
09.45-10.00	**ABC OR035**	**Elisa Gaggero**	*Removal of contaminants of emerging concern by enzymatic treatment with fungal laccases*
10-10.15.00	**ABC OR036**	**Giulia Guerra**	*Zinc and Iron Based Metal-Organic Frameworks as Ofloxacin Adsorbents in Polluted Waters*
10.15-10.30	**ABC OR037**	**Giuseppe Mascolo**	*Biodegradability enhancement of non-ionic surfactants in industrial wastewater by UV/H2O2 pre-treatment*

10.30-10.45	**ABC OR038**	**Giuseppe Mascolo**	*Remediation of groundwater contaminated with PCBs and PAHs by photocatalysis employing nano-sized TiO2 supported onto steel mesh*
10.45-11.00	**ABC OR039**	**Mirco Volanti**	*Biogas to Syngas through the Combined Steam/Dry Reforming Process: An Environmental Impact Assessment*
11.00-11.15			
11.15-11.30			
11.30-11.45	**ABC OR040**	**Sapia Murgolo**	*Assessment of a sustainable biofilter technology for reducing the environmental spread of CECs and odour emissions*
11.45-12.00	**ABC OR041**	**Federica Piras**	*Vacuum-UV as pre- and post-treatment to biofiltration: a novel integrated treatment scheme for wastewater reuse*
12.00-12.15	**ABC OR042**	**Concetta Pironti**	*A study of the biocidal effectiveness of permaleic acid (PMA): new promising application in disinfection process*
12.15-12.30	**ABC OR043**	**Annarosa Gugliuzza**	*2D Materials Engineered Membranes for a New Vision on Water Desalination*
12.30-12.45	**ABC OR044**	**Giuseppe Vitola**	*Membrane biofunctionalization for pesticide removal in surface water and vegetative water*
12.45-13.00	**ABC OR045**	**Domenico Cipriano**	*Protocol implementation of odour Proficiency Tests (PTs)*

Divisione CHIMICA FARMACEUTICA (FAR)
FAR 05

09.30 - 10.00	**FAR KN005**	**Yimon Aye**	*Leveraging precision electrophile signaling toward drug discovery*
10.00 - 10.30	**FAR KN006**	**Antimo Gioiello**	*Enabling synthesis and technologies to develop bile acid- inspired lead compounds*
10.30 - 10.45	**FAR OR019**	**Francesca Ferlenghi**	*A sulfonyl fluoride derivative selectively inhibits EGFRL858R/T790M/C797S by covalent modification of the catalytic lysine*
10.45 - 11.00	**FAR OR020**	**Angelica Artasensi**	*Novel potential DPP IV/ CA II inhibitors for the treatment of Type 2 Diabetes*
11.00 - 11.30	**FAR KN007**	**Andrea Stevenazzi**	*The selective inhibition of histone deacetylase 6 (HDAC6)*
11.30 - 11.45	**FAR OR023**	**Giannamaria Annunziato**	*Investigational studies on cyclopropane− carboxylic acid derivatives targeting O acetylserine sulfhydrylase as colistin adjuvants*
11.45 - 12.00	**FAR OR024**	**Simone Lucarini**	*Phenotype screening of a bisindole chemical library identifies URB1483 as a new antileishmanial agent with topoisomerase IB as molecular target*

12.00 - 12.15	**FAR OR025**	**Santo Previti**	*Development of peptidyl Michael acceptors for S3 pocket investigation of rhodesain, cysteine protease of Trypanosoma brucei rhodesiense*
12.15 - 12.30	**FAR OR026**	**Valentina Straniero**	*Development of benzodioxane-benzamides inhibitors of FtsZ as potent broad-spectrum antimicrobial agents*
12.30 - 13.00	**FAR KN008**	**Anna K.H. Hirsch**	*Addressing underexplored anti-infective targets*

FAR 06

10.30 - 10.45	**FAR OR021**	**Maria Dichiara**	*Design, synthesis and pharmacological evaluation of 4-carbamothioylphenyl sigma-1 receptor antagonists for pain treatment*
10.45 - 11.00	**FAR OR022**	**Giacomo Rossino**	*Identification of novel Sigma 1 receptor antagonists based on arylalkanolamine scaffold for the treatment of neuropathic pain*
11.00 - 11.30			
11.30 - 11.45	**FAR OR027**	**Marilena Muraglia**	*To042: prospective lead compound for the treatment of myotonic syndromes*
11.45 - 12.00	**FAR OR028**	**Sebastiano Intagliata**	*Development of mutual prodrugs of 5-fluorouracil and heme oxygenase 1 inhibitor as anticancer agents*
12.00 -12.15	**FAR OR029**	**Luca Pinzi**	*LigAdvisor: a web server to perform in silico explorations on crystallographic ligands and known drugs for polypharmacology and drug repurposing*
12.15 -12.30	**FAR OR030**	**Lucilla Turco**	*NMR contributions to process chemistry sustainability in the pharmaceutical research area*

Divisione CHIMICA FISICA (FIS)

FIS 06

Physical Chemistry for Biomedical Applications III

09:30-10:00	**FIS KN006**	**Debora Scuderi**	*Free electron Laser and IRMPD spectroscopy*
10:00-10:15	**FIS OR052**	**Rita Gelli**	*Insights into biologically-relevant calciprotein particles: effect of stabilizing agents on the formation and crystallization mechanisms*
10:15-10.30	**FIS OR053**	**Alessandra Del Giudice**	*Regulation of the photosynthetic AB-GAPDH via self-assembly*
10:30-10.45	**FIS OR054**	**Davide Tocco**	*Investigation of Fe-BTC and Z MOFs as carrier for Aspergillus.sp Laccase*
10:45-11:00	**FIS OR055**	**Pasquale Sacco**	*Biopolymer-based platforms for cell mechanosensing and regenerative medicine*

11:00-11.15	**FIS OR057**	**Marta Penconi**	*Advancing near-IR phosphorescence with Ir(III) complexes bearing a single emitting ligand: properties and OLED applications*
11.15-11.45	**break**		

Sessione congiunta con TEO

11:45-12:00	**FIS OR058**	**Fabio Gabas**	*Divide and Conquer Semiclassical Initial Value Representation: a valuable theoretical tool for vibrational spectroscopy of biological systems*
12:00_12:15	**TEO OR011**	**Giacomo Saielli**	*A computational view of ionic liquid crystals*
12:15-12.30	**FIS OR060**	**Tommaso Giovannini**	*Energy-Based Molecular Orbital Localization in specific Molecular Regions*
12:30-12:45	**TEO OR012**	**Alessio Petrone**	*Electronic attosecond dynamics: Ab initio treatment of photo-induced excitonic states*
12:45-13:15	**FIS KN007**	**George Froudakis**	*Designing Novel Nanoporous Materials for Applications in Energy and Environment. From Multi-Scale Modeling to Materials Informatics*

FIS 07

Sessione congiunta con CSB

09:30-10:00	**FIS KN008**	**Roland Winter**	*Temperature, Pressure, and Cosolute Effects on Liquid–Liquid Phase Separation and Condensates of Proteins: Physical Chemistry and Biological Implications*
10:00-10:15	**FIS OR067**	**Francesca Baldelli**	*Superfluorinated Exosomes for Sensitive in Vivo Tracking by 19F-MRI*
10:15-10.30	**FIS OR063**	**Cristina Carucci**	*Drug loaded polymer coated silica nanoparticles as drug delivery route against bacteria*
10:30-10.45	**FIS OR064**	**Francesca Biscaglia**	*Engineered Peptides on Gold Nanostructures for Enhanced Targeting Activity in Cancer Diagnosis*
10:45-11:00	**FIS OR065**	**Ilaria Clemente**	*Cubic and lamellar mesophases obtained from algal biomass as drug carriers with high potentiality*
11:00-11.15	**CSB OR026**	**Angelo Spinello**	*Small-molecule modulators of spliceosome-mutant cancers as a new therapeutic strategy against hematologic malignancies*
11:15-11.30	**CSB OR027**	**Nunzia laccarino**	*Effects of sequence and base composition on the CD and TDS profiles of i DNA*
11.30-11.45	**break**		

Sessione congiunta con ELE

11:45-12:15	**FIS KN009**	**Maria Vittoria Dozzi**	*CuWO4-based photoanodes for solar energy conversion: effects of Mo6+ doping and coupling with BiVO4*
12:15-12:30	**ELE OR038**	**Gennaro Sannino**	*Development of SnO2 composites as electron transport layer in un-encapsulated CH3NH3PbI3 solar cells*

12:30-12:45	**FIS OR069**	**Guillermo Escolano Casado**	*Cu-functionalized hydroxyapatites: a study of their physico-chemical properties and their potential as electrocatalysts*
12:45-13:00	**ELE OR039**	**He Xiufang**	*Investigation of the mechanism of Pt3Fe3 clusters for the hydrogen evolution reaction and for the oxygen reduction reaction*
13:00-13:15	**FIS OR071**	**Simone Di Muzio**	*Thermodynamics of the hydrolysis of lithium salts: pathways to the inorganic SEI components*

Divisione CHIMICA INORGANICA (INO)

INO 04

9.30 - 9.50	**INO PZ002 (Premio Dottorato 2020)**	**Anna Dall'Anese**	*Palladium catalyzed copolymerizations: from ligand architecture to macromolecule microstructure*
9.50 - 10.10	**INO PZ003 (Premio Dottorato 2020)**	**Giacomo Picci**	*Novel supramolecular architectures based on weak interactions*
10.10 - 10.30	**INO PZ004 (Premio Dottorato 2020)**	**Fortuna Ponte**	*Anticancer drugs: a detailed computational analysis of "non classical" compounds mechanism of action*
10.30 - 10.45	**INO OR022**	**Andrea Biffis**	*Gold catalyzed direct alkyne hydroarylations in ionic liquids: a powerful tool in organic synthesis*
10.45 - 11.00	**INO OR023**	**Luca Conti**	*Ru(II) polypyridyl complexes as promising light-responsive agents for biological application*
11.00 - 11.15	**INO OR024**	**Filippo Campagnolo**	*Development of sustainable and green methodologies for homogeneous gold(I) catalysis*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR025**	**Matteo Atzori**	*Magneto-chiral dichroism in chiral molecular magnets*
11.45 - 12.00	**INO OR026**	**Stefano Scoditti**	*Anticancer and photophysical properties of a N^C^N-coordinated Pt(II) complex*
12.00 - 12.15	**INO OR027**	**Paolo Cleto Bruzzese**	*17O spin density studies of single-metal sites in Cu-CHA zeolites*
12.15 - 12.30	**INO OR028**	**Federica Santulli**	*A single catalyst for the synthesis and chemical depolymerization of polylactide*
12.30 - 13.00	**INO PZ005 (Premio Nasini 2020)**	**Enrico Ravera**	*Paramagnetic NMR in bioinorganic chemistry in the 'twenties*

INO 05

10.30 - 10.45	**INO OR029**	**Mauro Ravera**	*Pt(IV) bifunctional complexes as anticancer agents: "is this true glory?"*

10.45 - 11.00	**INO OR030**	**Alessia Giordana**	*Solid acid catalysts for glucose hydrolysis: quantification of Lewis and Brønsted acid sites using 2,6-dimethylpyridine*
11.00 - 11.15	**INO OR031**	**Giorgio Facchetti**	*New sp3 diphosphine-based rhodium catalysts for the asymmetric addition of aryl boronic acids to azaarenes*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR032**	**Marco Chino**	*Design of a miniaturized FeS4 protein*
11.45 - 12.00	**INO OR033**	**Paolo Centomo**	*Selectivity enhancement of coordinating solvents on the direct synthesis of hydrogen peroxide*
12.00 - 12.15	**INO OR034**	**Tania Pecoraro**	*Luminescent self-assemblies of Pt(II) complexes in vivo*
12.15 - 12.30	**INO OR035**	**Cristiana Cesari**	*Homometallic and heterometallic ruthenium hydride carbonyl cluster*

INO 06

10.30 - 10.45	**INO OR036**	**Andrea Rossin**	*Thiazole-based Metal-Organic Frameworks for applications in CO2 storage/utilization and luminescence sensing*
10.45 - 11.00	**INO OR037**	**Patrizio Campitelli**	*Amino-decorated zinc bipyrazolate MOFs, an example of carbon dioxide capture and reuse (CCR)*
11.00 - 11.15	**INO OR038**	**Giorgio Tseberlidis**	*Sol-gel deposition of Cu2XYS4 thin-films with tunable bandgap as absorbers for photovoltaic applications*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR039**	**Francesca Deganello**	*Recycling inorganic waste into sustainable materials for energy and environment*
11.45 - 12.00	**INO OR040**	**Damiano Ricciarelli**	*Energy vs charge transfer in manganese doped lead halide perovskites*
12.00 - 12.15	**INO OR041**	**Marco Bellini**	*Electrocatalysis for energy: from nanostructured to molecular approach*
12.15 - 12.30	**INO OR042**	**Chiara Domestici**	*Novel mononuclear and dinuclear Ir-Cp* complexes bearing phosphonate and carboxylate ancillary and anchoring ligands as homogeneous and heterogenized water oxidation catalysts*

Divisione ELETTROCHIMICA (ELE)

ELE 05

09.30 - 10.00	**ELE_KN34**	**Matteo Bonomo**	*NiO/ZrO2 nanocomposites as photocathodes of tandem DSCs with higher photoconversion efficiency with respect to parent single-photoelectrode p-DSCs*
10.00 - 10.15	**FIS_OR068**	**Giuseppe Arrabito**	*Inkjet Printing Quasi-Miscible Droplets for Pseudo-Planar Organic Heterojunctions*
10.15 - 10.30	**ELE_OR35**	**Alessandro Facchin**	*Oxygen Reduction Reaction monitoring at Iron Single Site Catalyst: Electrochemical Scanning Tunnelling Microscopy of Iron Octaethylporphyrin*
10.30 - 10.45	**FIS_OR070**	**Mariangela Curcio**	*Laser irradiation of Bio-waste derived carbon as anode for Li-ion batteries*

10.45 - 11.00	**ELE_OR36**	**Barbara Vercelli**	*Doping or Aggregation: the case of Conjugated Polyelectrolytes PCPDTBT-2SO3K and PCPDTBT-SO3K*
11.00 - 11.15	**FIS_OR130**	**Elena Messina**	*Electrochemical study of Smart Nanocarriers forImproved Corrosion Protection of Reinforced Concrete*
11.15 - 11.30	**ELE_OR37**	**Marco Malferrari**	*Light-Induced Electrochemical Processes at Semiconductor-Films/Water Interface Modulate Cell Redox Balance*

ELE 06

09.30 - 10.00	**ELE_KN40**	**Stefania Rapino**	*Cancer Metabolic Profile Detected by Scanning ElectroChemical Microscopy*
10.00 - 10.15	**ANA_OR137**	**Ilaria Ragazzini**	*A simple and industrially scalable method for making a PANI-modified cellulose touch sensor*
10.15 - 10.30	**ELE_OR42**	**Nikolaou Pavlos**	*Ultrasensitive Hepatitis B Virus whole genome detection by Electrochemiluminescence*
10.30 - 10.45	**ANA_OR136**	**Cosimino Malitesta**	*Electrosynthesised ion imprinted polymers in development of sensor for Cd(II) ions determination in water*
10.45 - 11.00	**ELE_OR44**	**Patrik Sfragano**	*A bicyclic peptide-based biosensor for the electrochemical detection of a cancer-related protease*
11.00 - 11.15	**ANA_OR134**	**Veronica Caratelli**	*A Paper-Based Electrochemical Device for the Detection of Pesticides Inspired by Nature: a Flower-Like Origami Biosensor*
11.15 - 11.30	**ELE_OR43**	**Silvia Comis**	*Determination of emerging contaminants with electrochemical sensors based on titania nanoporous films: effect of sol aging on their electrochemical performances*
11.30 - 11.45	**break**		
11.45 - 12.00	**ANA_OR135**	**Noemi Colozza**	*A multiparametric electrochemical device for degradation monitoring in reinforced concrete*
12.00 - 12.15	**ELE_OR41**	**Alessanra Zanut**	*DNA-based Nanoswitches: insights into electrochemiluminescence signal enhancement*

ELE 07

11.30 - 12.00	**ELE_KN045**	**Marta Feroci**	*Solvent-supporting electrolyte system in electrolysis: not only chemical environment and charge carrier*
12.00 - 12.15	**ELE_OR04 6**	**Angeloclaudio Nale**	*Interplay between porosimetric parameters, densitometric parameters and catalytic activities of "Core-Shell" ORR Electrocatalysts*
12.15 - 12.30	**ELE_OR04 7**	**Gioele Pagot**	*Ion Coordination and Dynamics in Ionic Liquid-based Electrolytes for Hybrid Al/Mg Batteries*
12.30 - 12.45	**ELE_OR04 8**	**Carpanese Maria Paola**	*Copper-based perovskite electrodes for reversible solid oxide cells*
12.45 - 13.00	**ELE_OR04 9**	**Duranti Leonardo**	*Multi-functional Fuel Electrode for Reversible Solid Oxide Cells*

Divisione CHIMICA PER LE TECNOLOGIE (TEC)

TEC 04

9.30 - 10.00	**TEC IL002**	**Lvova Larisa**	*Recent advances in potentiometric sensors for environmental purposes: from single ion-selective electrodes to multisensor analysis*
10:00 - 10:10	**TEC OR035**	**Moulaee Kaveh**	*A new electrochemical platform for fast and efficient determination of dominant non-psychoactive cannabinoids in Cannabis Sativa*
10:10 - 10:20	**TEC OR036**	**Ferlazzo Angelo**	*Crown ether functionalized graphene quantum dots as electrochemical and fluorescence based sensors for the selective detection of potassium and sodium ions*
10:20 - 10:30	**TEC OR037**	**Zribi Rayhane**	*Electrochemical and sensing properties of 2D-MoS2 nanosheets produced via liquid cascade centrifugation at different rate*
10:30 - 10:40	**TEC OR038**	**Bella Federico**	*Hybrid solar cells operating in aqueous environment*
10:40 - 10:50	**TEC OR039**	**Grisorio Roberto**	*A new synthetic approach for size-tunable and stable CsPbBr3 nanocubes with near-unity photoluminescence quantum yield*
10:50 - 11:00	**TEC OR040**	**Bortolami Martina**	*BMIm-BF4: a versatile ionic liquid for BF3 generation and reactions*
11:00 - 11:15	**Discussion**		

Divisione TECNOLOGIA FARMACEUTICA (TFA)
TFA 02

09.30 - 10.00	**TFA IL003**	**Mauro Bonini**	*Release in oral solid nutraceutical forms: case studies.*
10.00 - 10.30	**TFA IL004**	**Marco Fidaleo**	*A lesson from Vitamin B12: from the biological issues to the design of a nutraceutical formulation*
10.30 - 10.45	**Discussion**		
10.45 - 11.00	**break**		
11.00 - 11.15	**TFA OR010**	**Annalisa Bianchera**	*Crystallization of stable doped mannitol polymorphs and in vitro assessment of their safety as carriers for lung delivery*
11.15 - 11.30	**TFA OR011**	**Luca Casula**	*Multicomponent nanosuspension for the bronchial asthma inhalation therapy*
11.30 - 11.45	**TFA OR012**	**Luca Cerri**	*Spray patch based on hyaluronic acid and chitosan microparticles medicated with olive leaf extract*
11.45 - 12.00	**TFA OR013**	**Maria Chiara Cristiano**	*EtoGel: combined systems for new ethosomes application in joint diseases treatments*
12.00 - 12.15	**TFA OR014**	**Tiziana Esposito**	*Castanea sativa waste as dermo-functional ingredient into a topical delivery system: from the design and development of the formulation to in vitro stability and in vivo skin tolerability and efficacy*
12.15 - 12.30	**TFA OR015**	**Diego R. Perinelli**	*Development of topical formulations using hydrolyzed keratin as an alternative to the commonly employed emulsifying agents*

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12.30 - 12.45	**TFA OR016**	**Teresa Silvestri**	*Biodegradable microparticles for the treatment of the posterior eye segment diseases*
12.45 - 13.00	**TFA OR017**	**Elena Giuliano**	*Poloxamer– and poloxamine-based hydrogels as biocompatible systems for the delivery of active compounds*
13.00 - 13.15	**TFA OR018**	**Umberto M. Musazzi**	*Printing of cutaneous patches loaded with propranolol for the treatment of infantile hemangiomas*

Programma dei LAVORI di DIVISIONE - 17 settembre pomeriggio

Divisione CHIMICA ANALITICA (ANA)

ANA 07

15.00 - 15.20	**ANA PZ003**	**Mariosimone Zoccali**	*Is There a Real Need for Multidimensional Chromatography Strategies with the Current Availability of Powerful Mass Spectrometry Platforms?*
15.20 - 15.40	**ANA KN008**	**Giovanni Ventura**	*AllerT: a Matlab-based workflow for putative allergens identification in novel foods via LC-ESI-MS/MS analysis*
15.40 - 16.00	**ANA OR051**	**Domenica Mangraviti**	*Differentiation and profiling of Morocco species belonging to Lamiaceae Family by Ambient Mass Spectrometry methods*
16.00 - 16.15	**ANA OR052**	**Nicole Marittimo**	*Advancements in Direct-MS using SPME coupled to Liquid-EI and CI*
16.15 - 16.30	**ANA OR053**	**Katia Arena**	*Characterization of bioactive compounds from natural products using focusing-modulated comprehensive two-dimensional liquid chromatography coupled to mass spectrometry*
16.30 - 16.45	**ANA OR054**	**Eleonora Oliva**	*Analysis of phenolic compounds in plant matrices by means of HPLC-MS/MS with targeted and semi-untargeted approach*
16.45 - 17.00	**ANA OR055**	**Tania Salerno**	*The Coupling of Gas Chromatography - Mass Spectrometry with Infrared Spectroscopy for Reliable Identification of Unknowns in Complex Samples*
17.00 - 17.15	**ANA OR056**	**Danilo Sciarrone**	*Reliability of monodimensional vs multidimensional GC-C-IRMS data: a critical evaluation*
17.15 - 17.30	**ANA OR057**	**Peter Q. Tranchida**	*Options of 1D GC, flow-modulation signal-enhanced 1D GC and flow-modulation comprehensive 2D GC in a single instrument: a proof-of-concept study*
17.30 - 17.45	**ANA OR058**	**Cecile Valsecchi**	*Enhanced LC-MS/MS spectra matching through multi-task neural networks and molecular fingerprints*

ANA 08

15.20 - 15.40	**ANA IL005**	**Alessandra Bianco Prevot**	*Organic Pollutant Removal using Photo-Fenton Processes in the presence of Fe(III) complexing agents*
15.40 - 16.00	**ANA IL006**	**Paola Fermo**	*In-situ and micro-destructive investigation for the analysis of degradation products present on marble surfaces*
16.00 - 16.15	**ANA OR059**	**Francisco Ardini**	*Evaluation of potential source areas for atmospheric lead reaching Ny-Ålesund (Svalbard) from 2010 to 2019*
16.15 - 16.30	**ANA OR060**	**Stefano Bertinetti**	*Strontium isotopic analysis of microsamples by inductively coupled plasma - tandem mass spectrometry*

16.30 - 16.45	**ANA OR061**	**Luca Carena**	*Photochemistry of furfuryl alcohol in/on snow at -30°C: photoreactivity with singlet oxygen and by direct photolysis*
16.45 - 17.00	**ANA OR062**	**Silvia Illuminati**	*Year-round records of bulk aerosol composition over the Victoria Land (Antarctica)*
17.00 - 17.15	**ANA OR063**	**Elisa Calà**	*Identification of aloe and other dyes by means of SERS and HPLC-DAD-MS in the embroidery of a 15th century English folded almanac*
17.15 - 17.30	**ANA OR064**	**Emilio Catelli**	*Rediscovering the lost color. Advanced vector quantization algorithm and hyperspectral imaging for digital restoration of color films*
17.30 - 17.45	**ANA OR065**	**Giovanna Marussi**	*The Third-Century monetary crisis: chemical analysis of Denarii and Antoniniani*
17.45 - 18.00	**ANA OR066**	**Rosaria Anna Picca**	*Synthesis and spectroscopic characterization of synergistic nanomaterials for stone artwork protection*

ANA 09

15.20 - 15.40	**ANA KN009**	**Paolo Bollella**	*Enzyme based Amperometric Biosensors: From Direct Electron Transfer to Chimeric Enzymes*
15.40 - 16.00	**ANA OR067**	**Giuseppe Arrabito**	*Printing Biology: engineering analytical platforms by molecular inks*
16.00 - 16.15	**ANA OR068**	**Noemi Bellassai**	*Design of dual-functional polymer on plasmonic biosensor for detection of circulating tumor DNA point mutations*
16.15 - 16.30	**ANA OR069**	**Alessandro Bertucci**	*Artificial Biomolecular Communication Regulated by Synthetic DNA Translators*
16.30 - 16.45	**ANA OR070**	**Alessandra Maria Bossi**	*Soft molecularly imprinted nanoparticles for protein recognition in sensing and assays*
16.45 - 17.00	**ANA OR071**	**Stefano Cinti**	*A microfluidic paper-based chip patterned with Prussian Blue to determine sweat urea*
17.00 - 17.15	**ANA OR072**	**Erica Del Grosso**	*Transient control of DNA-based systems*
17.15 - 17.30	**ANA OR073**	**Marco Giannetto**	*Smart immunosensors for point-of-care serologic test to determine the level of immunity by Covid-19 infection or by SARS-CoV-2 vaccination*
17.30 - 17.45	**ANA OR074**	**Antonia Lopreside**	*Reagent-free paper biosensor based on genetically modified bioluminescent protein for cancer biomarker detection*
17.45 - 18.00	**ANA OR075**	**Lucia Sarcina**	*Selective detection of Xylella fastidiosa with a Surface Plasmon Resonance based immunoassay*

Divisione CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI (ABC)

ABC 04

15.00-15.15	**ABC OR051**	**Dominique Scalarone**	*CAPuS project: research and higher education allied for the Conservation of Art in Public Spaces*

15.15-15.30	**ABC OR013**	**Ilaria Serafini**	*Advances in analytical methodologies applied to cultural heritage: first application of DLLME to characterize dyes in ancient textiles*
15.30-15.45	**ABC OR014**	**Slimani Sawssen**	*Caput Mortuum purple hematite pigment: Investigation of magnetic properties*
15.45-16.00	**break**		
16.00-16.15	**ABC OR015**	**Andrea Brunelli**	*Colloidal behavior of titanium dioxide nanoparticles in artificial and in Venice lagoon waters in the presence of standard or natural colloidal particles*
16.15-16.30	**ABC OR016**	**Felice Simeone**	*Assessment of the Cytotoxicity of Metal oxide Nanoparticles on the Basis of Immediately Available Physical-Chemical Parameters.*
16.30-16.45	**ABC OR017**	**Cristina De Ceglie**	*The effect of a karst-fractured aquifer on wastewater quality: an UHPLC-HRMS study*
16.45-17.00	**ABC OR018**	**Francesco Saliu**	*Plastic and its associated contaminants: determination of PAEs in coral reef invertebrates by in vivo SPME-LC-MS/MS*
17.00-17.15			
17.15-17.30	**ABC OR019**	**Armando Zarrelli**	*Characterization of degradation byproducts of Sartans: elucidation of their degradation pathway and ecotoxicity assessment*
17.30-17.45	**ABC OR020**	**Marco Mantovani**	*Microalgal treatment of the liquid fraction from hydrothermal carbonization process (HTC) in a circularity perspective*
17.45-18.00	**ABC OR021**	**Giulia Guidotti**	*Poly(diethylene 2,5-furanoate): a biobased promising candidate for compostable high-performant packaging*
18.00-18.15	**ABC OR022**	**Valeria D'Ambrosio**	*Lipids extraction from sewage sludge using green biosolvent for a sustainable production of biodiesel*

Divisione CHIMICA INDUSTRIALE (IND)

IND 04

Sessione congiunta con Gruppo Interdivisionale Energie Rinnovabili - Enerchem

15.00 - 15.30	**IND KN005 Chini Lecture**	**Carlo Perego**	*CO2 utilization: from waste to resource*
15.30 - 15.40	**IND OR033**	**Martina Serafini**	*Nanostructured Cu-based Electrocatalysts on a Carbonaceous Gas Diffusion Layer for the Electrochemical Reduction of CO2*
15.40 - 15.50	**IND OR034**	**Simelys Hernandez**	*How to exploit thermochemical catalysts to make efficient & sustainable CO2 electroreduction to added value products*
15.50 - 16.00	**IND OR035**	**Ivan Grigioni**	*High rate CO2 electroreduction to formate with a InP colloidal quantum dots derived catalyst*
16.00 - 16.10	**IND OR036**	**Federico Bella**	*Preliminary investigation of anodic materials for potassium batteries*
16.10 - 16.20	**IND OR037**	**Maria Grazia Musolino**	*Solvothermal synthesis of doped hematite/reduced graphene oxide nanocomposites for sodium-ion batteries*

16.20 - 16.30	**IND OR038**	**Emilia Paone**	*Reductive Upgrading of Biomass Derived Furan promoted by Spent Lithium-Cobalt Batteries as an Efficient Heterogeneous Catalyst*
16.30 - 16.40	**IND OR039**	**Matteo Bonomo**	*Thermosetting polyurethanes resins: application as cheap, sustainable and scalable encapsulants for (flexible) Perovskite Solar Cells*
16.40 - 16.55	***Discussion***		
16.55 - 17.10	**break**		
17.10 - 17.20	**IND OR040**	**Andrea Fasolini**	*Low Temperature Methane Steam Reforming in a H2-selective Pd Membrane Reactor*
17.20 - 17.30	**IND OR041**	**Tiziano Montini**	*Visible-light-driven coproduction of diesel precursors and hydrogen from lignocellulose-derived methylfurans*
17.30 - 17.40	**IND OR042**	**Nicola Sangiorgi**	*Improved water stability of CsPbBr3 thin film photoelectrodes*
17.40 - 17.50	**IND OR043**	**Cosimo Micheletti**	*Luminescent Solar concentrators based on Aggregation-Induced Emission*
17.50 - 18.00	**IND OR022**	**Giuseppe Pipitone**	*Aqueous phase reforming of biorefinery by-products towards sustainable hydrogen production*
18.00 - 18.10	**IND OR045**	**Francesco Conte**	*H2 production by photoreforming of glucose*
18.10 - 18.30	***Discussion***		

Divisione CHIMICA ORGANICA (ORG)
ORG 08

15.00 - 15.30	**ORG PZ006**	**Daniela Montesarchio**	***Premio alla ricerca Chimica Organica per le Scienze della Vita*** *G-Quadruplexes to the fore: towards DNA-targeting magic bullets*
15.30 - 16.00	**Break**		
16.00 - 16.15	**ORG PZ014**	**Anna Esposito**	***Premio Tesi di Dottorato Chimica Organica per le Scienze della Vita*** *Exploring the therapeutic potential of L-deoxyiminosugars in rare diseases*
16.15 - 16.30	**ORG OR045**	**Cristina Minnelli**	*Epigallocatechin-3-gallate-based Inhibitors Targeting EGFR to Overcome Drug Resistance in Advanced NSCLC*
16.30 - 16.45	**ORG OR046**	**Lucía Morillas Becerril**	*Specific and nondisruptive interaction of guanidium-functionalized gold nanoparticles with neutral phospholipid bilayers*
16.45 - 17.00	**ORG OR047**	**Maria Luisa Navacchia**	*Dihydroartemisinin-bile acid hybridization as an effective approach to enhance dihydroartemisinin anticancer activity*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR048**	**Ferran Nieto Fabregat**	*Gram-negative bacteria LPS recognition by DC-SIGN*

17.45 - 18.00	**ORG OR049**	**Anna Notaro**	*Mimiviruses possess the biosynthetic pathways to produce bacteria-like sugars in a clade-specific manner*
18.00 - 18.15	**ORG OR050**	**Alessandro Palmioli**	*On-cell saturation transfer difference NMR for the identification of FimH ligands and inhibitors*
18.15 - 18.30	**ORG OR051**	**Daniela Perrone**	*Synthesis and preclinical evaluation of antisense oligonucleotides conjugated with ursodeoxycholic acid for the treatment of Duchenne muscular dystrophy*

ORG 09

16.00 - 16.15	**ORG PZ013**	**Mirko Maturi**	***Premio Tesi di Dottorato Chimica Organica per l'Ambiente, l'Energia e le Nanoscienze*** *Advanced Functional Organic-Inorganic Hybrid (Nano)Materials: from Theranostics to Organic Electronics and Additive Manufacturing*
16.15 - 16.30	**ORG OR052**	**Mariacecilia Pasini**	*Sustainable by Design Carbon Dots as promising material for luminescent and biomedical applications*
16.30 - 16.45	**ORG OR053**	**Vincenzo Patamia**	*A new hybrid porous multifunctional material based on Loofah-Halloysite*
16.45 - 17.00	**ORG OR054**	**Marina Massaro**	*Synthesis and characterization of different mussel inspired materials for several applications*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR055**	**Giulia Neri**	*Fluorinated Polymers and Fluorescent Graphene as Innovative Nanotheranostic Materials*
17.45 - 18.00	**ORG OR056**	**Alessandra Operamolla**	*Cellulose nanocrystals for paper consolidation*
18.00 - 18.15	**ORG OR057**	**Luca Pettazzoni**	*Transamidation-based vitrimers from renewable sources*
18.15 - 18.30	**ORG OR058**	**Serena Riela**	*Improvement of properties of halloysite and some other «friends» by chemical modifications*

ORG 10

16.00 - 16.15	**ORG OR059**	**Claudio Curti**	*Merging Vinylogy with Organocatalysis: Direct, Asymmetric Entry to Chiral Fused Uracil Derivatives*
16.15 - 16.30	**ORG OR060**	**Daniele Fiorito**	*Synthetic studies towards Bastimolide B*
16.30 - 16.45	**ORG OR061**	**Paola Costanzo**	*Highly oleophilic and reusable polyurethane composites for the removal of oils from fresh water and seawater*
16.45 - 17.00	**ORG OR062**	**Andrea Mezzetta**	*Reactive Deep Eutectic Solvents (ReDESs): an underexploited option for organic chemistry*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR063**	**Lorenzo Di Terlizzi**	*Visible light-driven α-arylation of enol silyl ethers via arylazo sulfones.*

17.45 - 18.00	**ORG OR064**	**Lucia Ferrazzano**	*Greening peptide synthesis: new options for a sustainable chemistry*
18.00 - 18.15	**ORG OR065**	**Valeria Nori**	*Organocatalysed Michael addition of masked acetaldehyde to nitroalkenes in water*
18.15 - 18.30	**ORG OR066**	**Rita Mocci**	*Mechanochemical Fischer Indolisation: Exploration of a Timeless Reaction in a New Guise*

ORG 11

16.00 - 16.15	**ORG OR067**	**Allegra Franchino**	*Merging organo- and Au(I) catalysis for asymmetric or silver-free reactions of alkynes*
16.15 - 16.30	**ORG OR068**	**Gianluigi Albano**	*Infrared irradiation-assisted solvent-free Palladium-catalyzed (hetero)aryl-aryl coupling via C-H bond activation*
16.30 - 16.45	**ORG OR069**	**Fabio Bellina**	*Pd/Ag-mediated dehydrogenative alkynylation of imidazoles*
16.45 - 17.00	**ORG OR070**	**Silvia Gaspa**	*Photocatalyzed amides synthesis from alcohols by visible light*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR071**	**Fabrizio Medici**	*Stereoseletive [2+2] photocycloaddition: a viable strategy for the synthesis of enantiopure cyclobutane derivatives*
17.45 - 18.00	**ORG OR072**	**Francesco Messa**	*Ligand-Free Cobalt-Catalyzed Cross-Coupling Reaction Between Organoaluminum Reagents and (Hetero)Aryl and Alkyl Bromides*
18.00 - 18.15	**ORG OR073**	**Giorgia Zanchin**	*Imino-pyridine Cr complexes as precatalyst for the polymerization of olefins: synthesis and catalytic tests with NEt3 as additive*

Divisione CHIMICA DEI SISTEMI BIOLOGICI (CSB)

CSB 03

15.00 - 15.30	**CSB KN003**	**Luc Brunsveld**	*Stabilization of Protein-Protein Interactions; from the fundamentals of cooperativity to applications in drug discovery*
15.30 - 15.45	**CSB OR014**	**Alessio Romerio**	*Design, synthesis and Biological evaluation of New, glycolipid-based Toll-Like Receptor 4 (TLR4) Modulators*
15.45 - 16.00	**CSB OR015**	**Giusy Tassone**	*Evidence of amino-thiadiazoles as innovative inhibitors of human glutaminyl cyclase, validated target for neurodegenerative disorders*
16.00 - 16.15	**CSB OR016**	**Francesco Tadini-Buonisegni**	*Modulation of Ca2+-ATPase transport activity by pharmacologically relevant compounds*
16.15 - 16.30	**CSB OR017**	**Michela Pisani**	*Insulin loaded in liquid crystalline mesophases: effects on carrier structure and insulin stability*
16.30 - 17.00	**Break**		

17.00 - 17.30	**CSB KN004**	**Elena Sgaravatti**	*Research and development of active ingredients from vegetable cells or crops to be used in the Health care, Food and Personal care sectors*
17.30 - 17.45	**CSB OR018**	**Valeria Romanucci**	*New curcumin mimics based on tyrosol scaffold: investigation of neuroprotective and anticancer activity*
17.45 - 18.00	**CSB OR019**	**Roberto Tira**	*Modulation of Tau aggregation with natural coffee compounds*
18.00 - 18.10	**CSB OR020**	**Rita Pagano**	*Phosphate-linked Silybin dimers: synthesis and investigation of biological activity*
18.10 - 18.20	**CSB OR021**	**Massimiliano Gaeta**	*Hybrid Porphyrin/DOPA-melanin Film as Versatile Biomaterial for Water Remediation*
18.20 - 18.50	**Discussione**		

Divisione DIDATTICA CHIMICA (DID)
DID 02

15:00-15:30	**DID IL002**	**Carlo Fiorentini**	*The teaching of chemistry from the perspective of citizenship*
15:30-15:45	**DID OR010**	**Teresa Cecchi**	*Chemistry: a Precious Discovery in the Dantesque World*
15:45-16:00	**DID OR011**	**Maria Irene Donnoli**	*A Carbon atom journey*
16:00-16:15	**DID OR012**	**Elena Lenci**	*Peer review of scientific articles: a teaching experience*
16:15-16:30	**DID OR013**	**Silvia Prati**	*Increasing the engagement of non-chemistry major students: examples of didactic strategic*
16:30-18:30	**Panel Discussion**	**Silvia Bencivelli (coordinator) Pellegrino Conte Paola Govoni Piersandro Pallavicini Valentina Domenici**	*Chemistry: how, where, when and why*

Divisione SPETTROMETRIA DI MASSA (MAS)
MAS 02

15.00 - 15.40	**MAS PL003**	**Nikolai Kuhnert**	*Mass spectrometry in coffee science: From bean to drink to human*
15.40 - 16.10	**MAS KN001**	**Tata Alessandra**	*Non-targeted authentication of food products: the synergic combination of ambient mass spectrometry, data fusion and machine learning"*
16.10 - 16.25	**MAS OR006**	**M.A. Acquavia**	*Influence of mixed starter cultures of Hanseniaspora osmophila and Saccharomyces cerevisiae on wine flavor profile explored through HS-SPME/GC-MS*
16.25 - 16.35	**Break**		

16.35 - 17.05	**MAS KN002**	**Linda Monaci**	*Future challenges in MS based technologies applied to the safety of foods.*
17.05 - 17.20	**MAS OR007**	**Rosalia Zianni**	*Lipidomic approach to evaluate the effect of X-ray irradiation treatment on the lipid profile of Camembert cheese*
17.20 - 17.35	**MAS OR008**	**Fabiola De Marchi**	*High-resolution mass spectrometry approaches finalized to identification of new glycoside compounds in grape*
17.35 - 17.50	**MAS OR009**	**Ciro Cannavacciuolo**	*Analysis by high-resolution mass spectrometry of polyphenolic alkaloids fraction from Portulaca oleracea*
17.50 - 18.05	**MAS OR010**	**Lucia Bartella**	*Paper Spray tandem mass spectrometry: an innovative approach to assess flavonoid content in citrus drinks*

Divisione TEORICA E COMPUTAZIONALE (TEO)

TEO 02

15.00 - 15.30	**TEO KN002**	**Alfonso Pedone**	*Exploiting Machine Learning Methods in Atomistic Simulations of Oxide Glasses*
15.30 - 15.45	**FIS OR059**	**Adriana Pecoraro**	*First-principles study of Mn and Fe co-doped BaZrO3 as PC-SOFC cathode for the Oxygen Reduction Reaction*
15.45 - 16.00	**TEO OR013**	**Leonardo Guidoni**	*Quantum Chemistry using Quantum Computers*
16.00 - 16.15	**FIS OR061**	**Marco Medves**	*TDDFT methods for large systems: new computational schemes and automatic generation of density fitting basis*
16.15 - 16.30	**TEO OR014**	**Elena Tocci**	*Molecular view on crystals nucleation and growth on different PVDF polymorphs*
16:30 - 17:00	**Discussion**		

TEO 03

15:00 - 15:10	**TEO OR015**	**Matteo Capone**	*Multi-Scale Charge-Transfer Modeling in Enzyme Catalysis*
15:10 - 15:20	**TEO OR016**	**Guelber Cardoso Gomes**	*Computational study of dicationic ionic liquids based on imidazole*
15:20 - 15:30	**TEO OR017**	**Elisa Bernes**	*An experimental and theoretical investigation on the electronic structure of indole, 2,3-dihydro-7- azaindole, and 3-formylindole in the gas phase by synchrotron-based spectroscopic techniques*
15:30 - 15:40	**TEO OR018**	**Yasi Dai**	*Addressing the Frenkel and charge transfer character of exciton states with a model Hamiltonian based on dimer calculations: application to large aggregates of perylene bisimide*

17 settembre - pomeriggio

15:40 - 15:50	**TEO OR019**	**Stefano Motta**	*Study of ligand binding to HIF-2α through Path-Metadynamics*
15:50 - 16:00	**TEO OR020**	**Alessandra Gilda Ritacca**	*The multifaceted roles of copper ion in human body explored by computational tools*
16:00 - 16:10	**TEO OR021**	**Anna Rovaletti**	*Unravelling the reaction mechanism of Mo/Cu CO dehydrogenase using QM/MM calculations*
16:10 - 16:20	**TEO OR022**	**Sara Del Galdo**	*How water density responds to the presence of a crowding agent*
16:20 - 16:30	**TEO OR023**	**Francesco Ferdinando Summa**	*SYSMOIC: A Program Package for the Calculation of Origin-Independent Electron Current Density and Derived Magnetic Properties in Molecular Systems*
16:30 - 17:00	**break**		
17:00 - 17:20	**TEO KN003**	**Fabrizia Negri**	*Modelling extended-core π systems and their aggregates: charge transport and optoelectronic properties*
17:20 - 17:40	**TEO PZ003**	**Giovanni Di Liberto**	*Rational Design of Semiconductor Interfaces for Photocatalysis*
17:40 - 18:00	**TEO PZ004**	**Eduardo Schiavo**	*First Principles Approaches for Heterogeneous Functional Materials*
18:00 - 18:30	**Discussion**		

Programma dei LAVORI di DIVISIONE - 20 settembre mattina

Divisione CHIMICA ORGANICA (ORG)
ORG 12

9.30 - 10.00	**ORG PZ004**	**Pierangelo Gobbo**	***Medaglia Giacomo Ciamician*** *A synthetic chemistry approach to the fabrication of protocells and protocellular materials*
10.00 - 10.30	**ORG PZ007**	**Francesco Giacalone**	***Premio alla ricerca Chimica Organica per l'Ambiente, l'Energia e le Nanoscienze*** *Nanocarbon-based Hybrid Materials as Efficient and Sustainable Heterogeneous Catalysts*
10.30 - 10.45	**ORG OR074**	**Loredana Maiuolo**	*Polysubstituted 1,2,3-Triazoles: synthesis and biological application*
10.45 - 11.00	**ORG OR075**	**Michele Mancinelli**	*Atropisomeric Azaborines: Axial Chirality at the Boron-Carbon Bond*
11.00 - 11.15	**ORG OR076**	**Francesca Franco**	*Formal α-trifluoromethylthiolation of carboxylic acid derivatives via N-acyl pyrazoles*
11.15 - 11.30	**ORG OR077**	**Claudia Sciacca**	*Synthesis of nitrogenated analogues of honokiol as potential bioactive compounds*
11.30 - 11.45	**ORG OR078**	**Damiano Tanini**	*The unexpected role of Se(IV) vs Se(VI) species in the on water selenium-catalysed oxidation of anilines*
11.45 - 12.00	**ORG OR079**	**Claudio Zippilli**	*Double strategies for regioselective one-pot C-H oxidative functionalization of coumarins*

ORG 13

10.30 - 10.45	**ORG OR080**	**Chiara Liliana Boldrini**	*Eco-friendly deep eutectic solvent electrolyte solutions for dye-sensitized solar cells*
10.45 - 11.00	**ORG OR081**	**Gabriella Buscemi**	*Polydopamine/ethylenediamine nanoparticles embedding a bacterial photoenzyme for solar energy conversion*
11.00 - 11.15	**ORG OR082**	**Mattia Forchetta**	*Design of KuQuinone-Co3O4 nanoparticle hybrid dyads for photoelectrochemical applications*
11.15 - 11.30	**ORG OR083**	**Giulio Goti**	*Fluorescent Materials for the Enhancement of the Photosynthetic Efficiency*
11.30 - 11.45	**ORG OR084**	**Norberto Manfredi**	*Photo(electro)catalytic water splitting using Calix[4]arene-Based dyes*
11.45 - 12.00	**ORG OR085**	**Lorenzo Zani**	*Construction of tailored, donor-acceptor heterocyclic compounds for solar energy conversion*

ORG 14

10.30 - 10.45	**ORG OR086**	**Achille Antenucci**	*How do arenediazonium salts behave in Deep Eutectic Solvents? A combined experimental and computational approach*
10.45 - 11.00	**ORG OR087**	**Laura Baldini**	*Halogen-bonded architectures of multivalent calix[4]arenes*
11.00 - 11.15	**ORG OR088**	**Daniele Del Giudice**	*pH Transient Variation Triggered by Nitroacetic Acid Allowing Dissipative Control in Supramolecular Systems*
11.15 - 11.30	**ORG OR089**	**Oscar Francesconi**	*A tweezers-shaped receptor for the biomimetic recognition of the GlcNAc2 disaccharide in water*
11.30 - 11.45	**ORG OR090**	**Giorgio Olivo**	*Supramolecular Remote C(sp3)-H Oxidation*
11.45 - 12.00	**ORG OR091**	**Daniele Rosa-Gastaldo**	*Tuning the folding properties of synthetic recognition-encoded oligomers*

Programma dei LAVORI di DIVISIONE - 21 settembre mattina

Divisione CHIMICA DELL'AMBIENTE E DEI BENI CULTURALI (ABC)

ABC 05

09.30-09.45	**Presentation**		
09.45-10.00	**ABC OR046**	**P. Guzmán García Lascurain**	*Agar foam for the cleaning of art surfaces: a new approach*
10.00-10.15	**FIS OR 129**	**David Chelazzi**	*pHEMA/PAA and pHEMA/PVP semi-IPNs: physico-chemical characterization and use for bronze cleaning*
10.15-10.30	**FIS OR128**	**Francesco Armetta**	*Unusual corrosion of bronze helmets discovered in Mediterranean seabed*
10.30-10.45	**ABC OR047**	**Francesca Ramacciotti**	*Advanced systems for the cleaning of Cultural Heritage*
10.45-11.00	**FIS OR 127**	**Leonardo Severini**	*Ultrasound-stimulated PVA microbubbles as removal tool for adhesive tapes from cellulose-based materials*
11.00-11.15	**ABC OR048**	**Elisabetta Zendri**	*Evaluation of a new setup to improve the electro-kinetic desalination of porous materials in Cultural Heritage*
11.15-11.30			
11.30-11.45		**break**	
11.45-12.00	**ABC OR049**	**Marco Valente Chavez Lozano**	*Deep Eutectic Solvents (DES) based on choline chloride and betaine for cleaning gelatin residues from cellulose nitrate cinematographic films.*
12.00-12.15	**ABC OR050**	**Giuseppe Lazzara**	*Halloysite nanotubes: a versatile material for conservation of cultural heritage*
12.15-12.30	**ABC OR012**	**Francesca Nardelli**	*Insights into the oil paint polymeric network by Solid State NMR*
12.30-12.45	**ABC OR031**	**Carolina Rigon**	*Discovering the Maya ritual practices through the study of pigmented human bones remains by Archaeometry investigation*
12.45-13.00		**Antonio Marcomini**	*Conclusioni*

ABC 06

09.30-09.50	**ABC KN002**	**Fabrizio Passarini**	*The tool of LCA to analyse and improve the sustainability of chemical processes*
09.50-10.00	**IND OR046**	**Prisco Prete**	*New biodegradable catalysts for photo-Fenton like process for wastewater treatment reuse in a circular economy perspective*

10.00-10.10	**ABC OR053**	**Damiano Sgherza**	*Integrating biodegradation and ozone-catalysed oxidation for treatment of biomass gasification wastewater*
10.10-10.20	**IND OR047**	**Stefano Andrea Balsamo**	*One-pot synthesis of TiO2-rGO photocatalysts for the degradation of groundwater pollutants*
10.20-10.30	**ABC OR054**	**Luisa Barbieri**	*An integrated system for a new controlled release fertilizer based on lightweight ceramic aggregates starting from waste materials and bio-products*
10.30-10.40	**IND OR048**	**Ermelinda Falletta**	*Efficient day-and-night NO2 abatement by polyaniline/TiO2 composites*
10.40-10.50	**ABC OR055**	**Pietro Calandra**	*Reutilization of residues from municipal wastes pyrolysis to improve and regenerate asphalts*
10.50-11.00	**Discussion**		

Modellazione ambientale e caratterizzazione chimica degli aerosol atmosferici/Environmental

11.15-11.30	**ABC OR056**	**Loris Calgaro**	*Exposure modelling of emerging contaminants in the Venice lagoon - a case-study on active pharmaceutical ingredients*
11.30-11.45	**ABC OR057**	**Federtica Zennaro**	*Modelling eutrophication processes in the Venice Lagoon: a multivariate Machine Learning approach*
11.45-12.00	**ABC OR058**	**Pierluigi Barbieri**	*Bioaerosol detection, pathogen airborne transmission and abatement studies: capacity building, experimental results and perspectives from the COVID-19 pandemic*
12.00-12.15	**ABC OR059**	**Manuel Amedeo Cefali**	*Evaluation of PMx chemical composition and planning of a vegetable-green barrier in a high traffic site in Milan*
12.15-12.30	**ABC OR060**	**Niccolo Losi**	*Aerosol characterization from the tropics to the North Pole*
12.30-12.45	**ABC OR061**	**Alessandro Mancini**	*X-Ray Diffraction of Non-Exhaust Emissions generated from Braking: How to Assess the Phase Composition of the Crystalline Fraction*
12.45-13.00		**Antonio Marcomini**	*Conclusioni*

Divisione CHIMICA FARMACEUTICA (FAR)

FAR 07

09.30 - 10.00	**FAR KN009**	**Anders Bach**	*Targeting protein-protein interactions involved in oxidative stress using fragment-based drug discovery*

21 settembre - mattina

10.00 - 10.30	**FAR KN010**	**Giancarlo Aldini**	*Chemical and molecular mechanisms of cellular and extra-cellular antioxidants*
10.30 - 10.45	**FAR OR031**	**Marco Catto**	*A second life for MAO inhibitors: from CNS diseases to cancer*
10.45 - 11.00	**FAR OR032**	**Stefano Sainas**	*Apoptotic and differentiating therapy for AML using potent human dihydroorotate dehydrogenase inhibitor*
11.00 - 11.30	**FAR KN011**	**Tiziano Bandiera**	*Discovery of a picomolar potency corrector of F508del-CFTR chloride channel*
11.30 - 11.45	**FAR OR035**	**Francesca Spyrakis**	*Identification of carbapenemase broad-spectrum inhibitors through in silico methodologies*
11.45 - 12.00	**FAR OR036**	**Serena Massari**	*1,2,4-Triazolo[1,5-a]pyrimidines: efficient one-step synthesis and functionalization as antiviral agents*
12.00 -12.15	**FAR OR037**	**Alessandra Altomare**	*An integrated metabolomic and proteomic approach for the identification of covalent inhibitors of the main protease (Mpro) of SARS- COV-2 from crude natural extracts*
12.15 -12.30	**FAR OR038**	**Antonella Messore**	*Discovery of non-DKA derivatives endowed of selective activity against ribonuclease H function of the HIV-1 reverse transcriptase*
12.30 - 13.00	**FAR KN012**	**Pedro Gois**	*Exploring B-complexes as likers for targeting drug conjugates*

FAR 08

10.30 - 10.45	**FAR OR033**	**Claudia Sorbi**	*Constrained 1,4-dialkylpiperazines as dopamine transporter (DAT) inhibitors to fight psychosis and cocaine addiction*
10.45 - 11.00	**FAR OR034**	**Elisa Uliassi**	*Psychotropic-based bifunctional compounds for neurodegenerative diseases*
11.00 - 11.30			
11.30 - 11.45	**FAR OR039**	**Salvatore Di Maro**	*Peptides from bench to clinical studies: our experience with CXCR4*
11.45 - 12.00	**FAR OR040**	**Azzurra Stefanucci**	*A novel β-hairpin peptide derived from the ARC repressor selectively interacts with the major groove of B-DNA*
12.00 -12.15	**FAR OR041**	**Stefano Tomassi**	*Shading the activity of a CXCR4-interacting peptide by 1,4- and 1,5-disubstituted [1,2,3]-triazole-based cyclization*

12.15 -12.30	**FAR OR042**	**Rosa Bellavita**	*Grafting Temporin L peptides: old tactics for new antimicrobial weapons*

Divisione CHIMICA FISICA (FIS)

FIS 08

Cultural Heritage and Environment

09:30-10:00	**FIS KN010**	**Gabriella Di Carlo**	*Corrosion protection in Concrete Heritage: from material design to in situ validation*
10:00-10:15	**FIS OR072**	**Lorenzo Lisuzzo**	*Pickering Emulsions Based on Wax and Halloysite Nanotubes for the Treatment of Archeological Woods*
10:15-10.30	**FIS OR073**	**Vanessa Rosciardi**	*Biocomposite Poly(Vinyl Alcohol)/Starch cryogels: green tailorable tools for the cleaning of painted artworks*
10:30-10.45	**FIS OR074**	**Rosangela Mastrangelo**	*Cleaning Pollock's and Picasso's masterpieces: the physical chemistry behind the scenes*
10:45-11:00	**FIS OR075**	**Giovanna Poggi**	*Adaptive castor-oil based organogels: synthesis, characterization and use for the selective and controlled cleaning of works of art*
11:00-11.15	**FIS OR076**	**Michele Baglioni**	*Nanostructured Fluids For Polymeric Coatings Removal: Surfactants Affect the Polymer Glass Transition Temperature*
11:15-11.30	**FIS OR077**	**Sara Morandi**	*Pd-promoted zeolites for low-temperature NOx adsorption*
11.30-11.45	**break**		

Physical Chemistry of Sensors

11:45-12:00	**FIS OR078**	**Lucio Litti**	*Surface Enhanced Raman Scattering toward applications*
12:00_12:15	**FIS OR079**	**Stefano Toffanin**	*Organic optoelectronic components in highly integrated systems for plasmonics sensing in food security/quality*
12:15-12.30	**FIS OR080**	**Simona Bettini**	*SERS-SPR COUPLING FOR ULTRASENSITIVE DETECTION OF DOPAMINE IN ARTIFICIAL CEREBROSPINAL FLUID.*
12:30-12:45	**FIS OR081**	**Cristina Chirizzi**	*A bimodal imaging probe for combined Raman microscopy and 19F-MRI*
12:45-13:00	**FIS OR082**	**Giovanni De Filpo**	*Novel pressure sensors based on elastomeric PDLC films*
13:00-13:15	**FIS OR083**	**Francesco Tavani**	*Investigating the interfacial solvation properties of the Mg2+ ion by operando soft X-ray absorption spectroscopy at ambient pressure and simulations*

FIS 09

Physical Chemistry of Materials I

09:30-10:00	**FIS KN011**	**Luciano Galantini**	*From Molecules to Supracolloidal Atomium like Superstructures: Building from the Bottom-Up with Steroidal Amphiphiles*
10:00-10:15	**FIS OR084**	**Mario Prosa**	*Organic light-emitting transistors: advanced materials and innovative architectures towards a real-setting application*
10:15-10.30	**FIS OR085**	**Pietro Calandra**	*Mixing liquid amphiphiles to prepare organic fluids fully responsive to a magnetic field*
10:30-10.45	**FIS OR086**	**Valerio Loianno**	*A Hyphenated Approach Combining Pressure-Decay and In Situ FT-NIR Spectroscopy to Monitor Penetrant Sorption and Concurrent Swelling in Polymers*
10:45-11:00	**FIS OR087**	**Maria Rosaria Plutino**	*Design and development of multifunctional hybrid surface coatings for advanced and smart applications on textiles*
11:00-11.15	**FIS OR088**	**Federico Begni**	*Hyper Cross - Linked Polymers as additives for preventing aging of PIM1 membranes*
11:15-11.30	**FIS OR089**	**Chiara Nomellini**	*WO3-BiVO4 heterojunction: effects of WO3 nanostructuring on the photoelectrochemical performance*

Physical Chemistry of Materials II

11:45-12:00	**FIS OR090**	**Alberto Girlando**	*Charge-Transfer Soft Ferroelectrics*
12:00_12:15	**FIS OR091**	**Marco Sanna Angotzi**	*Designing Spinel Ferrite-Based Nano-Heterostructures Through Versatile Solvothermal Approaches*
12:15-12.30	**FIS OR092**	**Stefano Alberti**	*Physico-Chemical Characterization of Polydimethylsiloxane Electrospun Fibers*
12:15-12.30	**FIS OR051**	**Alessandro Piovano**	*A deep description of the electronic properties of Ti sites in Ziegler-Natta catalysts from advanced spectroscopic methods*
12:45-13:00	**FIS OR094**	**Matteo Busato**	*Structural Characterization of Deep Eutectic Solvents Mixtures with Water and Methanol*
13:00-13:15	**FIS OR095**	**Michele Porto**	*Use of REOBs and industrial by-products additives for new bitumen-like material formulation: chemical physical and mechanical characterization*

Divisione CHIMICA INORGANICA (INO)

INO 07

9.30 - 10.50	**INO PZ006 (Premio Dottorato 2021)**	**Fabio Pirro**	*De novo design of multi-domain metalloenzymes*
9.50 - 10.10	**INO PZ007 (Premio Dottorato 2021)**	**Matteo Vanni**	*Reactivity of Black Phosphorus with Pd Compounds*
10.10 - 10.30	**INO PZ008 (Premio Dottorato 2021)**	**Alessandra Barbanente**	*Targeted Delivery of Anticancer Platinum Complexes to Bone Tumors and Metastases "non classical" compounds mechanism of action*
10.30 - 10.45	**INO OR043**	**Rita Mazzoni**	*Cyclopentadienone-NHC Iron(0) electrocatalysts for water oxidation*
10.45 - 11.00	**INO OR044**	**Anna Pintus**	*Ammonium salts of oxalic acid derivatives: a new family of agents for the conservation of carbonate stone substrates of artistic value*
11.00 - 11.15	**INO OR045**	**Andrea Fermi**	*Visible-light activated metallaphotoredox catalysis enabled by TiIV complexes: new routes for C-C bond formation*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR046**	**Riccardo Pedrazzani**	*Correlating solid-state analysis and catalysis: exploring secondary π-interactions effects in Au(I) catalyzed reactions*
11.45 - 12.00	**INO OR047**	**Rossana Galassi**	*When metallaphilia makes the difference: the case of stacked coinage metals Trinuclear Cyclic Compounds*
12.00 - 12.15	**INO OR048**	**Alessia Belloni**	*FTIR-HSI analysis of triple-negative breast cancer (TNBC)*
12.15 - 12.30	**INO OR049**	**Francesca Gambassi**	*A Cu(II)-MOF based on a propargyl carbamate-functionalized isophthalate ligand*
12.30 - 13.00	**INO IL002**	**Anke Weidenkaff**	*Circular Materials for the Energy Transition*

INO 08

10.30 - 10.45	**INO OR050-ad hoc**	**Marzio Rancan**	*Hierarchical chiral transfer in bright lanthanides quadruple stranded helicate-cages by host-guest interaction*
10.45 - 11.00	**INO OR051**	**Giuseppe Ferrauto**	*Hydrophobic interactions between macrocyclic Gd-complexes and polyaromatic systems as route to enhance the longitudinal water relaxivity in Magnetic Resonance Imaging*

11.00 - 11.15	**INO OR052**	**Salvatore Impemba**	*Dinuclear Thioether-amide Aluminum Complexes in the Ring Opening Polymerization of Cyclic Esters*
11.15-11-30	**break**		
11.30 - 11.45	**INO OR053**	**Paolo Pelagatti**	*Put light on inside a microporous MOF to decipher the guest arrangement and guest- release properties*
11.45 - 12.00	**INO OR054**	**Francesca Garello**	*Biodegradable polyelectrolyte/magnetite capsules for MR imaging and magnetic targeting of tumors*
12.00 - 12.15	**INO OR055**	**Letizia Liccardo**	*CeOx/TiO2 Hollow Spheres as efficient photocatalyst for the degradation of organic pollutants in wastewater*
12.15 - 12.30	**INO OR056**	**Denise Lovison**	*Highly active ruthenium complexes: synthesis and evaluation of the anticancer activity through interaction with relevant biomolecules*

INO 09

10.30 - 10.45	**INO OR057**	**Gabriele Manca**	*Reactivity of imidazolate Au(I) cyclictrinuclearcompounds, CTCs, with iodine or MeI: a computational/experimental study*
10.45 - 11.00	**INO OR058**	**Luca Andreo**	*DFT and semi-empirical GFN2-xTB methods: experimental and computational characterization of an Iron(II) carbene complex*
11.00 - 11.15	**INO OR059**	**Mario Prejanò**	*How lanthanide ions affect the catalytic activity of methanol dehydrogenase: a computational point of view*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR060-ad hoc**	**Daniela Marasco**	*Transition metal complexes as neurodrugs: insights into their modulation of amyloid aggregation*
11.45 - 12.00	**INO OR061**	**Laura Del Coco**	*X. fastidiosa affecting olive trees in Salento: metal ions in soil, plants and treatment compounds*
12.00 - 12.15	**INO OR062**	**Antonino Famulari**	*Unveiling electronic and structural properties of, peroxygenase-like cytochrome P450, CYP116B5hd*
12.15 - 12.30	**INO OR063**	**Davide Corinti**	*Elusive intermediates in the reactivity of platinum(IV) prodrugs: a new perspective on their bioactivation*

Divisione CHIMICA PER LE TECNOLOGIE (TEC)

TEC 05

09.30 - 10.00	**TEC IL003**	**Alessandro Gori**	*Liquid biopsy at the crossroads of chemistry and technology: the extracellular vesicles case study*

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10.00 - 10.15	**TEC KN003**	**Serena De Santis**	*Fourier transform IR micro-spectroscopy of biological tissues: a promising tool for diagnostic and assessment of tissue functionality.*
10.15 - 10.30	**TEC KN004**	**Andrea Melchior**	*Diclofenac adsorption on carbon-based nanomaterials: a molecular dynamics study*
10.30 - 10.40	**TEC OR041**	**Francesca Baldassarre**	*Utilization of biosourced materials in chemical nanotechnologies developing controlled release systems for human and plants health*
10.40 - 10.50	**TEC OR042**	**Paola Astolfi**	*Structural characterization and in-vitro anticancer activity of nanovectors for delivery of bioactive coumpounds*
10.50 - 11.00	**TEC OR043**	**Arianna Rossetti**	*3D integration of pH-cleavable drug-hydrogel conjugates on magnetically driven smart microtransporters*
11.00 - 11.10	**TEC OR044**	**Falcone Giovanni**	*Calcium Alginate hydrogels in Semi Solid Extrusion 3D printing: physico-chemical requirements for high printing performance*
11.10 - 11.30	**Discussion**		
11.30 - 11.40	**TEC OR045**	**Anita Ceccucci**	*Mixed oxide Cerium coating for improved titanium nanotubes bioactivity*
11.40 - 11.50	**TEC OR046**	**Clelia Dispenza**	*Adipose stem cell spheroids-laden hydrogels for minimally invasive bone and cartilage regeneration interventions*
11.50 - 12.00	**TEC OR047**	**Emanuela Muscolino**	*k- Carrageenan and PVA blends as bioinks to 3D print scaffolds for cartilage reconstruction*
12.00 - 12.10	**TEC OR048**	**Edoardo Testa**	*Adducts of functionalized graphene layers with Ag nanoparticles for antimicrobial applications*
12.10 - 12.30	**Discussion**		
12.30 - 12.50	**break**		
12.50 - 13.00	**TEC OR049**	**Martina Sanadar**	*A novel luminescent Europium(III) complexes for citrate detection*
13.00 - 13.10	**TEC OR050**	**Gaspare Varvaro**	*Co/Pd-based synthetic antiferromagnetic multi-stacks for biomedical applications*
13.10 - 13.20	**TEC OR051**	**Alessandra Vitale**	*Coupling electrospinning and photo-induced crosslinking to produce shape-stable rubber nanofibrous membranes*
13.20 - 13.30	**TEC OR052**	**Antonino Rizzuti**	*Analysis of the chemical profile of sparkling wines fermented with autochthonous yeast strains using a non-targeted metabolomic approach*
13.30 - 13.50	**Discussion**		

13.50 - 14.00	**CONCLUSIONE**

Divisione ELETTROCHIMICA (ELE)

ELE 08

09.30 - 10.00	**ELE_IL50**	**Piotr Zelenay**	*Oxygen Reduction at Platinum Group Metal-Free Fuel Cell Catalysts:Piotr Recent Progress*
10.00 - 10.15	**ELE_OR51**	**Alessandro Facchin**	*From Redox-like to Heterogeneous Electrocatalysis at Metal-Octaethylporphyrins@HOPG investigated by EC-STM*
10.15 - 10.30	**ELE_OR52**	**Lucia Mazzapioda**	*Non-stoichiometric Metal Oxide Particles as Active Electrode Component in PEM Fuel Cells*
10.30 - 10.45	**ELE_OR53**	**Simone Bonizzoni**	*Aquivion®-based Alkaline Membrane for Fuel Cell and Electrolyzer Applications*
10.45 - 11.00	**ELE_OR54**	**Antunes Staffolani**	*Identification of Solid Oxide Cells Processes by Distribution of Relaxation Times: Model Creation and Validation*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELE_KN55**	**Lior Elbaz**	*Design of Aerogel-based Electrocatalysts for ORR*
11.45 - 12.00	**ELE_OR56**	**Davide Cademartori**	*Anode-supporting substrates with hierarchical porosity manufactured with freeze tape casting for reversible solid oxide cells*
12.00 - 12.15	**ELE_OR57**	**Vincenzo Baglio**	*Electrospun MnCo2O4/CNF as Oxygen Electrode for Alkaline Zn-Air Batteries*
12.15 - 12.30	**ELE_OR58**	**Eleonora Pargoletti**	*Disclosing the Electrocatalytic Behavior of Doped-MnO2 for Lithium-Air Batteries*

ELE 09

09.30 - 10.00	**ELE_IN59**	**Doron Auerbach**	
10.00 - 10.15	**ELE_OR60**	**Keti Vezzù**	*Innovative Olivine Cathodes for High-Voltage Lithium Batteries*
10.15 - 10.30	**ELE_OR61**	**Akiko Tsurumaki**	*Highly Versatile Gel Polymer Electrolytes for High Voltage Lithium Batteries*
10.30 - 10.45	**ELE_OR62**	**Marisa Falco**	*Protic ionic liquid electrolytes in lithium metal cells*
10.45 - 11.00	**ELE_OR63**	**Lorenzo Mezzomo**	*Long life lithium metal batteries employing dendrite-eating nanocomposite solid-state electrolytes based on hybrid fillers.*
11.00 - 11.15	**break**		

11.15 - 11.45	**ELE_KN64**	**Michele Pavone**	*Heterogeneous functional materials for post-Li energy storage devices, new insights and design principles from quantum chemistry*
11.45 - 12.00	**ELE_OR65**	**Ernestino Lufrano**	*Study of lithiated Nafion-based nanocomposites membranes as single lithium-ion conducting electrolytes for lithium batteries*
12.00 - 12.15	**ELE_OR66**	**Anna Mangini**	*Li-ion Batteries with Innovative Silicon Anodes: Study of Electrolytes Based on Carbonates*
12.15 - 12.30	**ELE_OR67**	**Alessandro Brilloni**	*Novel methods for increasing energy and reducing environmental impact of lithium batteries.*

ELE 10

09.30 - 10.00	**ELE_KN68**	**Tealdi Cristina**	*Fast but not so fast: can we improve intercalation in cathode materials for rechargeable batteries?*
10.00 - 10.15	**ELE_OR69**	**Toigo Christina**	*Rheological properties of aqueous sodium alginate slurries*
10.15 - 10.30	**ELE_OR70**	**Leonardo Sbrascini**	*Enhanced Performance of a Sustainable Si/C Anode for High Energy Density Lithium-ion Batteries*
10.30 - 10.45	**ELE_OR71**	**Daniele Versaci**	*Carbon nitride based double layer approach for enhancing Li-S battery performances*
10.45 - 11.00	**ELE_OR72**	**Hamideh Darjazi**	*Improvement of NMC layered cathode materials by combined doping/coating and evaluation of electronic-ionic transport properties by electrochemical impedance spectroscopy*
11.00 - 11.15	**break**		
11.15 - 11.45	**ELE_KN73**	**Teofilo Rojo**	*Recent progress in electrode materials for next generation sodium ion batteries*
11.45 - 12.00	**ELE_OR74**	**Giovanna Maresca**	*Sodium-conducting, ionic liquid electrolytes for Na battery systems*
12.00 - 12.15	**ELE_OR75**	**Shahid Khalid**	*Aqueous sodium battery enabled by super-concentrated binary electrolyte.*
12.15 - 12.30	**ELE_OR76**	**Michele Tribbia**	*Improved zinc electrodeposition in mild-acidic aqueous Zn-ion batteries*

Divisione TECNOLOGIA FARMACEUTICA (TFA)

TFA 03

09.30 - 10.00	**TFA IL005**	**Manuela Estima Gomes**	*Using magnetic stimulus to bioengineer tendon tissue and tissue models: new tools to understand and stimulate regenerative pathways*

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10.00 - 10.30	**TFA IL006**	**Marco Romanelli**	*Inflammation in wound healing: the role of drug delivery*
10.30 - 10.45	**Discussion**		
10.45 - 11.00	**break**		
11.00 - 11.15	**TFA OR019**	**Giuseppina Sandri**	*Polysaccharides based scaffolds for skin tissue engineering*
11.15 - 11.30	**TFA OR020**	**Giulia Vanti**	*Development and Optimisation of a Locally- acting Microemulgel to Improve the Biopharmaceutical Properties of Cannabidiol for Dermatological Delivery*
11.30 - 11.45	**TFA OR021**	**Silvia Pisani**	*Engineered tubular scaffold for full-thickness esophageal replacement*
11.45 - 13.30	**Tavola Rotonda**	**Michele Schlich**	*Valorizzazione del dottorato in tecnologia farmaceutica al di fuori dell'accademia. Cosa si aspetta un'azienda da un dottore di ricerca rispetto ad un laureato?*

Programma dei LAVORI di DIVISIONE - 21 settembre pomeriggio

Divisione CHIMICA ANALITICA (ANA)

ANA10

15.00 - 15.20	**ANA PZ004**	**Martina Catani**	*Boosting the downstream processing of biopharmaceuticals by means of multicolumn continuous chromatography*
15.20 - 15.40	**ANA IL007**	**Maurizio Quinto**	*Rotating Magnetic Chromatography, a new technique for micro-particle and cell separation*
15.40 - 16.00	**ANA IL008**	**Roccaldo Sardella**	*Role of mobile phase composition in enantioselective liquid chromatography*
16.00 - 16.15	**ANA OR076**	**Federica Bianchi**	*Nanomaterials for improved sensitivity in sample treatment*
16.15 - 16.30	**ANA OR077**	**Irene Coralli**	*Secondary reactions in the analysis of microplastics by Py-GC-MS*
16.30 - 16.45	**ANA OR078**	**Simona Felletti**	*Investigation of the chemoselectivity of normal phase stationary phases towards the separation of cannabinoids*
16.45 - 17.00	**ANA OR079**	**Giuseppina Gullifa**	*Potential Health Impact Assessment of New Pocket Pen- Vaporizers: Vapor Characterization Using SPME-GC/MS*
17.00 - 17.15	**ANA OR080**	**Jacopo La Nasa**	*Analytical pyrolysis coupled with gas chromatography/mass spectrometry and solvent extraction for the characterization of microplastics and polymer additives*
17.15 - 17.30	**ANA OR081**	**Roberta La Tella**	*Evaluation of carbon - clad zirconia columns as stationary phases for superheated water liquid chromatography*
17.30 - 17.45	**ANA OR082**	**Marcello Locatelli**	*Fabric Phase Sorptive Extraction: an innovative tool for TDM and pharmacotoxicological studies using unconventional biological matrices*
17.45 - 18.00	**ANA OR083**	**Sara Palmieri**	*Molecular imprinted polymer coupled to LC-MS/MS for maleic hydrazide determination in food samples*
18.00 - 18.15	**ANA OR084**	**Marco Roverso**	*Determination of lactose in low-lactose milk by direct liquid injection and high-resolution mass spectrometry*

ANA11

15.20 - 15.40	**ANA KN010**	**Silvia Berto**	*Study and application of chemical models to measure the urine saturation with calcium salts*
15.40 - 16.00	**ANA OR085**	**Chiara Abate**	*Sequestering ability of carnosine towards some potentially toxic divalent metal cations in aqueous solution*

16.15 - 16.30	**ANA OR087**	**Denise Bellotti**	*Understanding the thermodynamics and coordination chemistry of metal-binding proteins: the common thread to elucidate metal acquisition processes at host/pathogen interface*
16.30 - 16.45	**ANA OR088**	**Rosita Cappai**	*Complex formation equilibria of a kojic acid derivative with different metal ions*
16.45 - 17.00	**ANA OR089**	**Salvatore Cataldo**	*CYCLODEXTRIN-BASED NANOSPONGES FOR LEAD(II) ION ADSORPTION FROM AQUEOUS SOLUTIONS*
17.00 - 17.15	**ANA OR090**	**Ottavia Giuffrè**	*O-phosphorylethanolamine and O-phosphorylcholine in aqueous solution: acid-base behavior and speciation with Mg2+*
17.15 - 17.30	**ANA OR091**	**Anna Irto**	*Thermodynamic parameters on the interaction of divalent and trivalent metal cations with 3-hydroxy-4-pyridinones*
17.30 - 17.45	**ANA OR092**	**Luana Malacaria**	*Studies on the complexation between quercetin and some first-row transition metal cations in aqueous solution*
17.45 - 18.00	**ANA OR093**	**Rossella Migliore**	*Recognition of antibiotics by calixarene-based micellar aggregates in aqueous solution: binding features and driving forces*
18.00 - 18.15	**ANA OR094**	**Davide Spanu**	*On-line ion trapping by frontal chromatography ICP-MS: a low-cost strategy for the fast speciation of inorganic pollutants*

ANA12

15.20 - 15.40	**ANA KN011**	**Flavio Della Pelle**	*2D Nanomaterials: among functional natural compounds and affordable sensor designs*
15.40 - 16.00	**ANA KN012**	**Barbara Roda**	*Celector(R): the cell chromatography for quality control of living cells*
16.00 - 16.15	**ANA OR095**	**Jessica Brandi**	*Identification of protein biomarkers responsible for meat tenderness in bovine Longissumus dorsi muscle by Kohonen self-organizing maps and multivariate analysis*
16.15 - 16.30	**ANA OR096**	**Simone Cavalera**	*Anti-Retroviral Drugs Monitoring in Urine and Saliva: A Rapid and Sensitive Lateral Flow Immunoassay for Tenofovir*
16.30 - 16.45	**ANA OR097**	**Andrea Cerrato**	*An innovative analytical platform for cannabis chemovar differentiation based on untargeted metabolomics and chemometrics*

16.45 - 17.00	**ANA OR098**	**Angela Di Capua**	*Use of online buffer exchange coupled to native-mass spectrometry to elucidate the stoichiometry of the Salmonella FraR (transcriptional repressor)-DNA complex*
17.00 - 17.15	**ANA OR099**	**Fabio Di Nardo**	*Exploiting silver nanoplates as colorimetric label in Lateral Flow Immunoassay*
17.15 - 17.30	**ANA OR100**	**Nicolò Interino**	*UPLC-Q-TOF-MS/MS analysis of bile acids and their main metabolite profile in farm animal faeces and species-specific correlation with gut microbiota*
17.30 - 17.45	**ANA OR101**	**Valentina Marassi**	*Nanosphere, polymer, self-assembled material? Clearing up the confusion on polydopamine through multidetection-FFF*
17.45 - 18.00	**ANA OR102**	**Monica Mattarozzi**	*Insights into aptamer-protein interactions for analytical applications: egg white lysozyme as case study*
18.00 - 18.15	**ANA OR103**	**Lapo Renai**	*Untargeted metabolomics reveals different postprandial serum metabolome profiles after single intake of Vaccinium myrtillus and Vaccinium corymbosum*

Divisione CHIMICA INDUSTRIALE (IND)

IND 04

Sessione congiunta con Gruppo Interdivisionale Green Chemistry - Chimica Sostenibile

15.00 - 15.20	**IND KN006**	**Rafael Luque**	*Benign by design strategies for a more sustainable future: the valorisation concept*
15.20 - 15.30	**IND OR049**	**Anna Gagliardi**	*Upgrading of Ethanol: Boosting the Guerbet Reaction with a Redox Co-Catalyst*
15.30 - 15.40	**IND OR050**	**Ilenia Rossetti**	*Sustainable process design for the valorization of bioethanol as platform chemical*
15.40 - 15.50	**IND OR051**	**Maela Manzoli**	*Enabling technologies to boost cellulose selective valorisation over bifunctional catalyst*
15.50 - 16.00	**IND OR052**	**Silvia Tabasso**	*Green deep eutectic solvents and microwave technology towards a closed loop biorefinery*
16.00 - 16.10	**IND OR053**	**Nicola Di Fidio**	*Microwave-assisted FeCl3-catalysed production of glucose from giant reed and cardoon cellulose fraction and its fermentation to new generation oil by oleaginous yeasts*
16.10 - 16.20	**IND OR054**	**Alessia Ventimiglia**	*Theoretical study of glucose oxidation to glucaric acid using gold based catalyst*
16.20 - 16.35	***Discussion***		
16.35 - 16.50	**break**		
16.50 - 17.10	**IND KN007**	**Volker Hessel**	*Sustainability as Process Design Guidance for Flow and Plasma Chemistry*
17.10 - 17.20	**IND OR055**	**Valeria Pappalardo**	*Heterogeneous catalysis in the esterification of natural antioxidants*

17.20 - 17.30	**IND OR056**	**Carmelina Rossano**	*Amberlite IR120 as catalyst for the levulinic acid esterification reaction in batch and continuous operation*
17.30 - 17.40	**IND OR057**	**Silvia Giorgi**	*Synthesis of new biopolymers by biomasses valorization*
17.40 - 17.50	**IND OR058**	**Riccardo Bacchiocchi**	*Innovative heterogeneous catalysts for the reduction of levulinic acid derivatives to γ-valerolactone and consecutive reduction products*
17.50 - 18.00	**IND OR059**	**Francesco Mauriello**	*Hydrogenolysis of aromatic ethers under lignin-first conditions*
18.00 - 18.30	**Discussion**		

Divisione CHIMICA ORGANICA (ORG)
ORG 15

15.00 - 15.30	**ORG PZ002**	**Paolo Tecilla**	***Medaglia Angelo Mangini*** *Self-organized Supramolecular Systems for Catalysis, Sensing and Transport*
15.30 - 16.00	**ORG PZ009**	**Elena Lenci**	***Premio alla ricerca Chimica Organica per le Scienze della Vita Junior*** *Combining Diversity-Oriented Synthesis and chemoinformatics to generate small molecules libraries*
15.50 - 16.00	**Break**		
16.00 - 16.15	**ORG OR092**	**Molly Pither**	*Elucidation of the Chemical Structure of Lipopolysaccharides Isolated from the Commensal Bacteria Veillonella parvula*
16.15 - 16.30	**ORG OR093**	**Debora Pratesi**	*The glycomimetic approach for selective inhibition of Carbonic Anhydrases*
16.30 - 16.45	**ORG OR094**	**Deborah Quaglio**	*Resorc[4]arene-based site directed immobilization of antibodies for immunosensors development*
16.45 - 17.00	**ORG OR095**	**Roberto Rossi**	*Problem solving in Pharmaceutical processes: isolation, characterization and synthetic preparation of unknown impurities in 4-piperidinepropanol manufacture*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR096**	**Laura Russo**	*Chemoselective synthesis of triple-functionalizes nanoparticles for multimodal in vivo imaging of pancreatic β-cells*
17.45 - 18.00	**ORG OR097**	**Giovanni Sacco**	*Affinity enhancement of peptide ligands for tumor overexpressed receptors*
18.00 - 18.15	**ORG OR098**	**Cristina Manuela Santi**	*Synthesis of an analogue of Neisseria meningitidis A capsular polysaccharide for the development of a glycoconjugate vaccine*
18.15 - 18.30	**ORG OR099**	**Federica Santino**	*Rational Design of Pseudoproline-Containing K-Opioid Receptor-Selective Peptidomimetics*

ORG 16

15.30 - 16.00	**ORG PZ010**	**Manuel Orlandi**	***Premio alla ricerca Chimica Organica nei suoi Aspetti Metodologici Junior*** ***Catalyst Design via Computational Means:*** *Correlations Bridge Experiments and Calculations*
16.00 - 16.15	**ORG OR100**	**Valentina Pirota**	*Selective hydrolysis of water-soluble naphthalene diimides driven by core-substitution*
16.15 - 16.30	**ORG OR101**	**Simone Potenti**	*4-Fluorothreonine as a test case: the effects of fluorination on molecular properties*
16.30 - 16.45	**ORG OR102**	**Michele Ricci**	*Application of ASCA modelling tools on a PDO hard cheese: Analysis of the effects on physical parameters of Trentingrana*
16.45 - 17.00	**ORG OR103**	**Federica Sabuzi**	*Computational study of substituted phenols pKa*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR104**	**Carla Rizzo**	*New supramolecular fluorescent NDI-gels as bioimaging materials*
17.45 - 18.00	**ORG OR105**	**Maria Sologan**	*Functionalized gold nanoparticles for MRI applications*
18.00 - 18.15	**ORG OR106**	**Benedetta Maria Squeo**	*Thiophene substituted aza-BODIPY as promising metal-free, pure NIR emitter for OLEDs*
18.15 - 18.30	**ORG OR107**	**Kristian Vasa**	*Design and synthesis of macromolecular and nanostructured carbonic anhydrases-based materials*

ORG 17

15.30 - 16.00	**ORG PZ011**	**Sara Meninno**	***Premio alla ricerca Chimica Organica per l'Ambiente, l'Energia e le Nanoscienze Junior*** *Powerful Strategies to Functionalized Molecules in One- Pot, Mild Conditions and Benign Solvents*
16.00 - 16.15	**ORG OR108**	**Giulio Bertuzzi**	*Novel Visible-Light Mediated Protocols for the Synthesis of N Heterocycles and Site-Selective Functionalizations*
16.15 - 16.30	**ORG OR109**	**Tommaso Bortolato**	*Radical α-Trifluoromethoxylation of Ketones by Means of Organic Photoredox Catalysis*
16.30 - 16.45	**ORG OR110**	**Mattia Di Maro**	*A ball-milling green synthetic procedure for the preparation of novel macromolecular stabilizers for polyolefinic-based materials*
16.45 - 17.00	**ORG OR111**	**Salvatore Marullo**	*Cholinium-based ionic liquids as catalysts for the glycolysis of post-consumer PET waste*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR112**	**Angelica Mero**	*Treatment of biomass food waste by exploiting Natural Deep Eutectic Solvents and bio based-Ionic Liquids*

17.45 - 18.00	**ORG OR113**	**Elisabetta Monciatti**	*Hydroaminomethylation of terminal alkenes in water: microwave and micellar catalysis roles*
18.00 - 18.15	**ORG OR114**	**Matteo Tiecco**	*Organocatalytic activity of chiral L-Proline-based Deep Eutectic Solvents*
18.15 - 18.30	**ORG OR115**	**Federica Valentini**	*Catalytic biomass valorization towards hydrogen transfer reactions using formic acid and derivates as safe H-source*

ORG 18

15.30 - 16.00	**ORG PZ012**	**Nicolas D'Imperio**	***Premio alla ricerca Chimica Organica per lo Sviluppo di Processi e Prodotti nell' Industria Junior*** *Olefins from carbonyls. Development of new phosphorus-based cross-coupling reactions*
16.00 - 16.15	**ORG OR116**	**Valerio Fasano**	*How Big is the Pinacol Boronic Ester as a Substituent?*
16.15 - 16.30	**ORG OR117**	**Susanna Bertuletti**	*From carbonyls to chiral alcohols via asymmetric biocatalysis: exploiting the substrate promiscuity of hydroxysteroid dehydrogenases (HSDHs)*
16.30 - 16.45	**ORG OR118**	**Denisa Bisag**	*Catalyst- and substrate- dependent chemodivergent reactivity of stabilised sulfur ylides with salicylaldehydes*
16.45 - 17.00	**ORG OR119**	**Giulia Brufani**	*Imidazolium based heterogenous catalyst for the synthesis of cyanohydrintrimethylsylil ether and β-azido ketones*
17.00 - 17.30	**Break**		
17.30 - 17.45	**ORG OR120**	**Emanuela Calcio Gaudino**	*Highly Efficient Microwave-assisted synthetic protocols under Pd based β-cyclodextrin heterogeneous catalyst*
17.45 - 18.00	**ORG OR121**	**Francesco Calogero**	*Photoredox allylation and propargylation of aldehydes catalytic in titanium*
18.00 - 18.15	**ORG OR122**	**Vincenzo Campisciano**	*Al(III) Porphyrin–Imidazolium Salt Copolymer onto Carbon Nanotubes as Catalyst for the Synthesis of Cyclic Carbonates*
18.15 - 18.30	**ORG OR123**	**Francesca Foschi**	*Copper-Catalyzed/Hypervalent Iodine(III)-Mediated Dimerization/Cyclization of 2-Benzylamino-phenols: Synthesis of Fluorescent Oxazolo-phenoxazines*

Divisione CHIMICA DEI SISTEMI BIOLOGICI (CSB)

CSB 04

15.00 - 15.30	**CSB KN005**	**Angela Casini**	*Gold-templated reactions in biological systems: from medicine to catalysis*

15.30 - 15.45	**CSB OR022**	**Francesco Bellia**	*Hyaluronate–Carnosine conjugates: copper(II) complexes and antioxidant properties*
15.45 - 16.00	**CSB OR023**	**Daniele Vitone**	*The speciation of zinc complexes with chloroquine ligand*
16.00 - 16.15	**CSB OR024**	**Valentina Oliveri**	*8-Hydroxyquinoline Hybrids Differentially Interact with α-Synuclein*
16.15 - 16.30	**CSB OR025**	**Giancarlo Terraneo**	*Halogenation Dictates Architectures and Properties of Amyloid Peptides*
16.30 - 17.00	**Break**		
17.00 - 17.30	**CSB KN006**	**Amedeo Caflisch**	*Fragment-based drug design*
17.30 - 17.45	**FIS OR066**	**Federica Rizzi**	*Role of the FZD10 delivering exosomes in cellular proliferation of gastrointestinal cancer*
17.45 - 18.00	**FIS OR062**	**Ivana Miletto**	*Functionalized Upconversion Nanoparticles for Theranostic*
18.00 - 18.15	**CSB OR028**	**Gabriele Travagliante**	*Spectroscopic study on interactions of porphyrins and micro-RNA*
18.15 - 18.50	**Discussione**		

Divisione DIDATTICA CHIMICA (DID)
DID 03

15:00-15:30	**DID IL003**	**Eleonora Aquilini**	*Caring for yourself, the environment and others in primary school*
15:30-15:45	**DID OR014**	**Sergio Palazzi**	*Towards a material archive of dyestuffs from the XX century*
15:45-16:00	**DID OR015**	**Ugo Cosentino**	*The School-University joint interventions provided in the National Recovery and Resilience Plan*
16:00-18:00	**Panel Discussion**	**Riccardo Iacona (Coordinator)** **Vincenzo Balzani** **Andrea Segrè** **Vittorio Maglia** **Giovanni De Feo**	*360-degree sustainability*

Divisione SPETTROMETRIA DI MASSA (MAS)
MAS 03

15.00 - 15.40	**MAS PL004**	**Encarnación Moyano**	*Mass spectrometry for the environmental analysis of halogenated organic pollutants*
15.40 - 16.10	**MAS KN003**	**Sara Bogialli**	*Mass spectrometry for the monitoring and protection of the environment*
16.10 - 16.25	**MAS OR011**	**Carolina Barola**	*Temporal trend of per- and polyfluoroalkyl substances in air samples collected at the rural site of Monte Martano (Central Italy)*
16.25 - 16.35	**Break**		

16.35 - 17.15	**MAS PL005**	**Antony Memboeuf**	*How can energetics in CID MS/MS help the analytical chemists?*
17.15 - 17.30	**MAS OR012**	**Angela Tartaglia**	*Fabric Phase Sorptive Membrane Array: A Novel Approach for Non-Invasive In Vivo Sampling*
17.30 - 17.45	**MAS OR013**	**Raffaella Pascale**	*An interplay between FT-ICR MS and LC-LTQ MS/MS for Metabolic Profiling of Peperoni di Senise PGI Bell Peppers*
17.45 - 18.00	**MAS OR014**	**Eugenio Aprea**	*Volatile organic compounds in Gorgonzola cheese and their relationship with sensory descriptors and consumers' liking*
18.00 - 18.15	**MAS OR015**	**Flaminia Vincenti**	*New Synthetic Opioids: Development of Analytical Methods for Their Characterization and Determination by Means of HPLC-HRMS/MS*

Divisione TEORICA E COMPUTAZIONALE (TEO)
TEO 04

15:00 -15:20	**TEO KN004**	**Mauro Stener**	*Predictive optical photoabsorption of metal clusters via efficient TDDFT simulations*
15:20 - 15:40	**TEO PZ005**	**Lorenzo Cupellini**	*Multiscale investigation of chlorophyll fluorescence quenching in plant light-harvesting complexes*
15:40 - 15:50	**TEO OR024**	**Chiara Aieta**	*Quantum nuclear densities from semiclassical on-the-fly molecular dynamics*
15:50 - 16:00	**TEO OR025**	**Filippo Lipparini**	*An easy and efficient strategy to compute an accurate SCF guess for ab-initio molecular dynamics simulations*
16:00 - 16:10	**TEO OR026**	**Marco Mendolicchio**	*Accuracy and Reliability in the Simulation of Vibrational Spectra: A Comprehensive Benchmark of Generalized Vibrational Perturbation Theory to the Second Order (GVPT2)*
16:10 - 16:20	**TEO OR027**	**Fulvio Perrella**	*Improving accuracy and efficiency of ADMP Extended Lagrangian Molecular Dynamics*
16:20 - 16:30	**TEO OR028**	**Diego Sorbelli**	*Probing the electronic structure of gold dihydride with state-of-the-art relativistic approaches*
16:30 - 17:00	**break**		
17:00 - 17:20	**TEO PZ006**	**Nicola Tasinato**	*Computational Strategies for Environmental Chemistry*
17:20 - 17:30	**TEO OR029**	**Francesco Di Maiolo**	*Theoretical Approaches to Quantum Molecular Dynamics in Out of Equilibrium Environments*
17:30 - 17:40	**TEO OR030**	**Lorenzo Donà**	*Extending and assessing composite electronic structure methods to the solid state*
17:40 - 17:50	**TEO OR031**	**Federica Lodesani**	*An in-depth look into the mechanism of crystallization of lithium disilicate: a metadynamics study*

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17:50 - 18:00	**TEO OR032**	**D. K. Andrea Phan Huu**	*Molecular spectroscopy in condensed phases: an antiadiabatic approach to the medium polarizability*
18:00 - 18:10	**TEO OR033**	**Pierpaolo Pravatto**	*Tunneling splitting and the stochastic description of activated processes*
18:10 - 18:30	**discussione finale**		

Programma dei LAVORI di DIVISIONE - 23 settembre mattina

Divisione CHIMICA ANALITICA (ANA)

ANA13

09.30 - 09.50	**ANA IL009**	**Anna Laura Capriotti**	*The progress in peptidomics: new strategies for purification and untargeted identification of short peptides*
09.50 - 10.00	**break**		
10.00 - 10.15	**ANA OR104**	**Adriana Arigò**	*Analytical methods in clinical lipidomics: HPLC and SFC comparison for the analysis of lipid mediators in clinical samples*
10.15 - 10.30	**ANA OR105**	**Alfonsina D'Amato**	*nLC-MS/MS data integration of quantitative proteomics and lipidomics to study the effects of bioactive compounds*
10.30 - 10.45	**ANA OR106**	**Chiara De Luca**	*Multicolumn Countercurrent Solvent Gradient Purification (MCSGP) process for the intensification of the polishing step of a bioactive peptide mixture*
10.45 - 11.00	**ANA OR107**	**Dounia El Fadil**	*Enzyme inhibition coupled to Molecular Imprinted Polymers for acetazolamide determination in biological samples*
11.00 - 11.15	**ANA OR108**	**Alessio Lenzi**	*Determination of salivary short chain fatty acids and hydroxy acids in heart failure patients by in-situ derivatization and Hisorb-probe sorptive extraction coupled to thermal desorption and gas chromatography- tandem mass spectrometry*
11.15 - 11.30	**ANA OR109**	**Marcello Manfredi**	*Metaproteomics and metabolomics investigation of microbiome alterations in pediatric obese subjects*
11.30 - 11.45	**ANA OR110**	**Francesca Merlo**	*A simple and Fast Multiresidue Method for determination of hormones in vegetables and fruits*
11.45 - 12.00	**ANA OR111**	**Giuseppe Micalizzi**	*Microwave distillation technique for the isolation of Cannabis Sativa L. essential oils and GC-MS/FID analysis for terpenes and terpenoids characterization.*
12.00 - 12.15	**ANA OR112**	**Daniele Naviglio**	*"Cholesterol is not considered a nutrient of concern for overconsumption" (Dietary Guidelines for Americans 2015)*

ANA14

09.30 - 09.50	**ANA IL010**	**Nicola Cioffi**	*Analytical Challenges in the Fight Against Biological Threats. The case of Nanoantimicrobials Inhibiting the Persistency of SARS-CoV-2*
09.50 - 10.00	**break**	**break**	
10.00 - 10.15	**ANA OR113**	**Maria Luisa Astolfi**	*A rapid analytical method for the determination of 45 elements in extra-virgin olive oils*

10.15 - 10.30	**ANA OR114**	**Laura Barone**	*Innovative spectroscopic approach for bloodstains identification*
10.30 - 10.45	**ANA OR115**	**Deborah Biggio**	*Surface characterization of CuZn37 alloys in contact with artificial saliva: the role of organic compounds*
10.45 - 11.00	**ANA OR116**	**Beatrice Campanella**	*A multi-analytical approach for the study of immortalized hippocampal neurons after mild heat shock*
11.00 - 11.15	**ANA OR117**	**Roberta D'Agata**	*Ultrasensitive plasmonic assay and specifically-designed PNA probes for circulating microRNAs detection: towards a liquid biopsy*
11.15 - 11.30	**ANA OR118**	**Danilo Donnarumma**	*Identification and quantification of toxic compounds and essential molecules in the context of tuna fishery industry waste valorization*
11.30 - 11.45	**ANA OR119**	**Walter Giurlani**	*Film thickness determination of metal multilayers by XRF multivariate analysis using Monte Carlo simulated standards*
11.45 - 12.00	**ANA OR120**	**Giulia Gorla**	*Low-cost miniaturized NIR spectrometer as an analytical tool for monitoring kefir fermentation process*
12.00 - 12.15	**ANA OR121**	**Min Li**	*XAS study of Manganese Hexacyanoferrate cathode material in aqueous Zn-ion batteries at three K-metal edges*
12.15 - 12.30	**ANA OR122**	**Maria Chiara Sportelli**	*Analytical characterization of laser-ablated silver nanoparticles for safe and biodegradable food packaging applications*

ANA15

09.30 - 09.50	**ANA OR123**	**Raffaela Biesuz**	*SAFER Smart Labels at work on fish*
09.50 - 10.00	**break**		
10.00 - 10.15	**ANA OR124**	**Sara Gaggiotti**	*Liquid phase exfoliated Transition Metal Dichalcogenides for gas sensing*
10.15 - 10.30	**ANA OR125**	**Laura Montali**	*A clover-like paper biosensor for mercury (II) on-site monitoring with a combined bioluminescent-colorimetric detection*
10.30 - 10.45	**ANA OR126**	**Andrea Pastore**	*pH Colorimetric sensor Arrays based on acid-base indicators enhanced by surfactants*
10.45 - 11.00	**ANA OR127**	**Angela Punzo**	*Application of whole-cell analytical bioassay based on turn-on chemiluminescence dioxetane probe sensing to quantify intracellular H2O2 in nutraceutical and biomedical fields*
11.00 - 11.15	**ANA OR128**	**Simona Ranallo**	*Non-natural antibody-protein communication mediated by a synthetic DNA responsive device*

11.15 - 11.30	**ANA OR129**	**Annalisa Scroccarello**	*Colorimetric paper-based analytical device for direct evaluation of olive oil phenols*
11.30 - 11.45	**ANA OR130**	**Francesca Torrini**	*A competitive microplate bioassay to detect gonadorelin in urine samples via a polynorepinephrine-based molecular imprinted polymer*
11.45 - 12.00	**ANA OR131**	**Mohamad Ahmad**	*A spatial perspective to retrieve spatial-spectral signatures from overlapped components in spectroscopic imaging data*
12.00 - 12.15	**ANA OR132**	**Rosalba Calvini**	*Quantification of rind percentage in grated Parmigiano Reggiano cheese by NIR-hyperspectral imaging and evaluation of the effect of factors related to sample preparation and composition*
12.15 - 12.30	**ANA OR133**	**Eleonora Mustorgi**	*Multivariate online monitoring of a powder blending process using a miniaturized near infrared sensor*

Divisione CHIMICA FISICA (FIS)

FIS 10

Physical Chemistry of Biomaterials

09:30-10:00	**FIS KN012**	**Roberto De Santis**	*Design for biointerface engineering*
10:00-10:30	**FIS KN013**	**Julietta Rau**	*New trends in the development of biomedical implants with multifunctional surfaces*
10:30-10.45	**FIS OR096**	**Monica Dettin**	*Chitosan covalently functionalized with peptides mapped on Vitronectin and BMP-2 for bone tissue engineering*
10:45-11:00	**FIS OR097**	**Angela De Bonis**	*Study of the bioactivity of thin glass-ceramic films deposited on electrospun polymeric scaffolds by nanosecond PLD*
11:00-11.15	**FIS OR021**	**Lorenzo Degli Esposti**	*Crystallization of amorphous calcium phosphate to hydroxyapatite nanoparticles: new insights in the field of biomaterials and biomineralization*
11:15-11.30	**FIS OR099**	**Alessio Carmignani**	*Study of the impact of size on the properties of polydopamine nanoparticles and their interaction with glioblastoma multiforme cells*

Computational and Applied Chemistry

11.45-12.00	**FIS OR100**	**Laura Orian**	*Methylmercury toxicity: insight from a theoretical physical-chemical description*
12:00_12:15	**FIS OR101**	**Marta Corno**	*Ab-initio modelling of Fe2NiP-H2O interaction: a phosphate factory for Early Earth*
12:15-12.30	**FIS OR102**	**Mirko Leccese**	*First-principles study of the C/Si interface: the influence of graphene corrugation on the H adsorption and abstraction reactions*

12:30-12:45	**FIS OR103**	**Brunella Bardi**	*Excited-state symmetry breaking in an aza-nanographene dye*
12:45-13:00	**FIS OR104**	**Rosangela Santalucia**	*HCN adsorption and reactivity at the Mg2SiO4 surface:a laboratory model of the chemistry on interstellar dust grains*

FIS 11

Physical Chemistry for Environment and Materials I

09:30-10:00	**FIS KN014**	**Cataldo Simari**	*Reversible and low-cost CO2 capture by quaternary-ammonium-functionalized aromatic polymers*
10:00-10:15	**FIS OR105**	**Claudio Cara**	*High value-added mesostructured silica from hexafluorosilicic acid (FSA): from a hazardous waste to precious silicon source.*
10:15-10.30	**FIS OR106**	**Rodolfo Esposito**	*A sustainable approach to formulation chemistry:structure and dynamics of bio-based complex mixtures*
10:30-10.45	**FIS OR107**	**Mariafrancesca Baratta**	*Photocatalytic degradation of organic pollutants in water using an innovative TiO2/SWNT membrane*
10:45-11:00	**FIS OR108**	**Chiara Lo Porto**	*Plasma deposition of TiO2-based nanocomposite coating for photocatalytic degradation of organic pollutants in water*
11:00-11.15	**FIS OR110**	**Stefano Marchesi**	*The NMR relaxometry as a powerful tool to study the uptake of paramagnetic ions from water by synthetic saponite clays*
11:15-11.30	**FIS OR109**	**Giulia Siciliano**	*Synthesis and characterization of polydopamine coated SPIONs for Cu2+ ions removal of from water*
11.30-11.45	**break**		

Physical Chemistry for Environment and Materials II

11:45-12:00	**FIS OR111**	**Nicola Blangetti**	*Template assisted sol-gel synthesis of Fe-doped TiO2 with photocatalytic activity under visible light*
12:00_12:15	**FIS OR112**	**Chiara Nannuzzi**	*Physico-chemical characterization of high surface area TiO2*
12:15-12.30	**FIS OR113**	**Massimo Dell'Edera**	*Nano-TiO2 based material for environmental and antibacterial application*
12:30-12:45	**FIS OR114**	**Marco Montalbano**	*Combining Morphology, Surface Fluorination and Au Nanoparticles Deposition on TiO2: Effects on Rhodamine B Photodegradation*
12:45-13:00	**FIS OR115**	**Maria Francesca Colella**	*Chemical-physical methods to investigate properties of vegetable oils and fats*
13:00-13:30	***Conclusioni***		

FIS 12

Thermodynamics and Kinetics I

09:30-10:00	**FIS KN015**	**Andrea Scorciapino**	*Development of a thermodynamic and kinetic model for passivemigration of ion carriers across lipid bilayers*
10:00-10:15	**FIS OR116**	**Marco Paolantoni**	*When the Solute is Completely Slaved to the Solvent:Jump Reorientation of Formamide in Water*
10:15-10.30	**FIS OR117**	**Federico Rossi**	*Shape Transformation of Artificial Vesicles Induced by an Interplay between Osmosis and pH Change*
10:30-10.45	**FIS OR118**	**Martina Maria Calvino**	*Shelf-life prediction of paracetamol formulations by non-isothermal thermogravimetry*
10:45-11:00	**FIS OR119**	**Chiara Pelosi**	*Stability of protein-polymer conjugates in solution*
11:00-11.15	**FIS OR120**	**Stefano Salvestrini**	*Kinetics and mechanism of 4-hydroxybenzoic acid degradation by persulfate/MnO2 oxidation*
11:15-11.30	**FIS OR121**	**Valentina Migliorati**	*Unraveling the solvation properties of Lanthanide (3+) ions: from molecular solvents to Ionic Liquid based systems*

Thermodynamics and Kinetics II

11:45-12:00	**FIS OR122**	**Marcello Budroni**	*Between dissipative structure and applications: chemical oscillations*
12:00_12:15	**FIS OR123**	**Olga Russina**	*NATURE OF SOLVATION OF CYCLODEXTRINS IN (PROTIC) IONIC LIQUIDS AND DEEP EUTECTIC SOLVENTS*
12:15-12.30	**FIS OR124**	**Duccio Tatini**	*Specific ions effects in green oleate-based formulations: how salts can influence the structure and rheology of viscoelastic systems*
12:30-12:45	**FIS OR125**	**Marianne Moedlinger**	*Structures and phase equilibria in the ternary Cu-As-Sb system (a preliminary investigation)*
12:45-13:00	**FIS OR126**	**Alessandro Damin**	*Cu+ bi-pyridine based homoleptic complexes as catalysts for partial oxidation reactions: a Raman study*

Divisione CHIMICA INDUSTRIALE (IND)

IND 06

09.30 - 10.00	**IND KN008 Medaglia Mario Giacomo Levi**	**Siglinda Perathoner Gaetano Iaquaniello**	*Waste-to-chemicals: a low-carbon innovative solution for circularity*
10.00 - 10.10	**IND OR060**	**Stefania Lucantonio**	*Experimental study of interactions between biomass pellets and oxygen carriers for chemical looping gasification in fluidized beds*

10.10 - 10.20	**IND OR061**	**Lucia Fagiolari**	*Electrodes and electrolytes for aqueous dye-sensitized solar cell*
10.20 - 10.30	**IND OR062**	**Francesca Rosso**	*Carbon Dioxide Absorption Mechanism in Biocompatible Ionic Liquids Solutions*
10.30 - 10.40	**IND OR063**	**Giuliano Giambastiani**	*"To Dissipate or not to Dissipate extra-Heat? This Is the Question!" How to Reduce Energy Wastes in a Challenging Process at the Heart of P2G Chain*
10.40 - 10.50	**IND OR064**	**Matteo Borella**	*A study of Kraft lignin conversion and possible upgrading to valuable compounds*
10.50 - 11.05	***Discussion***		
11.05 - 11.20	**break**		
11.20 - 11.40	**IND KN009**	**Paolo Vacca**	*New generation of specialty zeolites for sustainable chemistry*
11.40 - 11.50	**IND OR065**	**Giorgio Ferrari**	*Multifunctional Hardening Accelerator for Low-Clinker Binders*
11.50 - 12.00	**IND OR066**	**Rosa Vitiello**	*Optimization of HASE polymers effect in formulation of cement using Design of Experiment*
12.00 - 12.10	**IND OR067**	**Matteo Guidotti**	*Are Aqueous Hydrogen Peroxide and Sodium Percarbonate Efficient in the Inactivation of SARS-CoV 2?*
12.10 - 12.20	**IND OR068**	**Carlo Pirola**	*Chemical Plants Active Learning by Virtual Immersive Laboratory: the Eye4edu Project*
12.20 - 12.30	**IND OR069 Premio Tesi di Dottorato**	**Veronica Papa**	*Manganese- and Cobalt Based Catalysts for Homogeneous Hydrogenation*
12.30 - 12.40	**IND OR070**	**Elena Ghedini**	*Biomasses, Drug Delivery and Hi-Tech formulative protocols*
12.40 - 12.50	**IND OR071**	**Maryam Hmoudah**	*Assessment of the robustness of iron-based metal organic framework (MIL-88A) in aqueous environment*
12.50 - 13.00	***Discussion***		

Divisione CHIMICA INORGANICA (INO)
INO 10

9.30 - 10.00	**INO PZ009 (Premio Malatesta)**	**Roberta Sessoli**	*The contribution of coordination chemistry to the second quantum revolution*
10.00 - 10.30	**INO PZ010 (Premio Nasini 2021)**	**Edoardo Mosconi**	*Computational Modeling of Perovskite for Photovoltaic Applications*
10.30 - 10.45	**INO OR064-ad hoc**	**Iole Venditti**	*Functionalized silver nanoparticles for water pollution monitoring: sensitivity, selectivity and the challenge of eco-safe behavior*

10.45 - 11.00	**INO OR065**	**Diego Tesauro**	*New aromatic NHC-gold complexes as anticancer agents: protein target evaluation and cytotoxic activity*
11.00 - 11.15	**INO OR066**	**Farid Hajareh Haghighi**	*Silane-functionalized TiO2 nanoparticles decorated with Ag nanoparticles for dual antimicrobial effects*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR067**	**Francesca Tessore**	*Porphyrins for second order nonlinear optics*
11.45 - 12.00	**INO OR068**	**Annaluisa Mariconda**	*Sulfonated N-heterocyclic carbene silver(I) and gold(I) water soluble complexes: catalytic and cytotoxic activity*
12.00 - 12.15	**INO OR069**	**Riccardo Freccero**	*Widening the tin solid-state chemistry: unusual bonding scenario in the LaMgSn2 rare-earth stannide*
12.15 - 12.30	**INO OR070**	**Veronica Ghini**	*NMR reveals the metabolic changes induced by Auranofin in ovarian cancer cells*
12.30 - 13.00	**INO IL003**	**David P. Giedroc**	*Metals, molecules and metabolism: Molecular mechanisms of bacterial metallostasis*

INO 11

10.30 - 10.45	**INO OR071**	**Antonio Zucca**	*Advances in Pt(II) rollover chemistry*
10.45 - 11.00	**INO OR072**	**Marco Lunardon**	*Hybrid transition metal dichalcogenide/graphene microspheres for hydrogen evolution reaction*
11.00 - 11.15	**INO OR073**	**Silvia Mostoni**	*Porphyrin functionalized ZnO/SiO2 hybrid nanoparticles as scintillator agent*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR074**	**Alfonso Annunziata**	*Square-planar vs. trigonal bipyramidal molecular geometry in glucoconjugate triazole Pt(II) complexes: synthesis, in-solution behaviour and anticancer properties*
11.45 - 12.00	**INO OR075**	**Giada Mannias**	*Iron(III) trimesate xerogel by ultrasonic irradiation*
12.00 - 12.15	**INO OR076**	**Christian Rossi**	*Exploiting the transformative features of metal halides for the synthesis of CsPbBr3@SiO2 core-shell nanocrystals*
12.15 - 12.30	**INO OR077**	**Luciano Marchiò**	*Supramolecular assemblies in silver bispyrazolylmethane complexes: phase transitions and the role of the halogen bond*

INO 12

10.30 - 10.45	**INO OR078**	**Adolfo Speghini**	*Fine-tuning of the size of luminescent CaF2 nanoparticles*
10.45 - 11.00	**INO OR079**	**Antonio Santoro**	*Responsive Self-Assembled Dynamic Helicates*
11.00 - 11.15	**INO OR080**	**Chiara Mazzariol**	*Synthesis in confined space of luminescent nanostructures of undoped and Eu(III)-doped calcium molybdate*
11.15-11.30	**break**		
11.30 - 11.45	**INO OR081**	**Marta Stucchi**	*The synergistic and photochromic effect of Au nanoparticles on a Silver-waste derived TiO2 photocatalyst*

11.45 - 12.00	**INO OR082**	**Diego Olivieri**	*Efficient palladium catalyzed bis-alkoxycarbonylation of olefins for the synthesis of useful succinic acid derivatives*
12.00 - 12.15	**INO OR083**	**Luca Rigamonti**	*Multivariate approach to the analysis of structural data of iron(II) spin crossover complexes and cobalt(II) single molecule magnets*
12.15 - 12.30	**INO OR084**	**Simonetta Geninatti**	*Histidine containing PLGA nanoparticles as novel theranostic agents for Boron Neutron Capture Therapy*

Divisione CHIMICA ORGANICA (ORG)
ORG 19

9.30 - 10.00	**ORG PZ003**	**Pierangelo Metrangolo**	***Medaglia Giorgio Modena*** *A Journey through the Word of Halogen Bonding*
10.00 - 10.30	**ORG PZ008**	**Jacopo Roletto**	***Premio alla ricerca Chimica Organica per lo Sviluppo di Processi e Prodotti nell'Industria*** *The art of Process Development in API manufacturing*
10.30 - 10.45	**ORG OR124**	**Andrea Sartori**	*Dual Conjugates Targeting αVβ3/αVβ6 Integrins and Tyrosine Kinase Receptors as antifibrotic agents*
10.45 - 11.00	**ORG OR125**	**Angela Scala**	*Synthesis and biological profile of novel three-arms star-shaped PLA-PEG amphiphilic copolymers*
11.00 - 11.15	**ORG OR126**	**Monica Scognamiglio**	*Isolation and structural elucidation of oleanane saponins from Bellis sylvestris Cyr. involved in plant-plant chemical interactions*
11.15 - 11.30	**ORG OR127**	**Alba Silipo**	*Herbaspirillum Root189 LPS glycan chain decorations affect LPS bioactivity, membrane properties and prevent plant immune recognition*
11.30 - 12.00	**Break**		
12.00 - 12.15	**ORG OR128**	**Laura Siracusa**	*Secondary metabolic profiles and anticancer actions from fruit extracts of immature pomegranates*
12.15 - 12.30	**ORG OR129**	**Rachele Stefania**	*Enhanced relaxivity by hydrophobic interactions of macrocyclic Gd-HPDO3A complexes linked to pyranine*
12.30 - 12.45	**ORG OR130**	**Luca Valgimigli**	*Oxygen Uptake Kinetics as a Powerful Tool to Investigate Tyrosinase Enzyme Inhibition*
12.45 - 13.00	**ORG OR131**	**Danilo Vona**	*Enzyme immobilization on polydopamine-coated living microalgae cells for bioremediation*

ORG 20

10.30 - 10.45	**ORG OR132**	**Matteo Corrieri**	*Metal-Free Synthesis of Azacarbolines Enabled by Hypervalent Iodine-Promoted Intramolecular Oxidative Cyclization*

10.45 - 11.00	**ORG OR133**	**Federico Frateloreto**	*Functionalization of C-H bond using self-assembling supramolecular iron(II) complexes*
11.00 - 11.15	**ORG OR134**	**Andrea Gualandi**	*Photoredox allylation of aldehydes mediated by bismuth and cobalt*
11.15 - 11.30	**ORG OR135**	**Marco Lombardo**	*Visible Light Photocatalytic Synthesis of Oxygenated Heterocyclic Compounds*
11.30 - 12.00	**Break**		
12.00 - 12.15	**ORG OR136**	**Michela Lupi**	*A Hydrogen Bond Donor / Lewis Base (HBD/LB) catalytic route to enantioenriched hetero[4]helicenes*
12.15 - 12.30	**ORG OR137**	**Giulia Martelli**	*Fast Heck-Cassar-Sonogashira Cross-Coupling Reactions with Palladium Catalyst Recycling and Green Solvent/Base recovery*
12.30 - 12.45	**ORG OR138**	**Silvia Gazzola**	*2- and 6-Purinylmagnesium Halides in Dichloromethane: Scope and Insights Into the Solvent Influence on the C- Mg Bond*
12.45 - 13.00	**ORG OR139**	**Angelo Nacci**	*Nanostructured catalysts for a circular economy*

ORG 21

10.30 - 10.45	**ORG PZ015**	**Gabriele Laudadio**	***Premio Tesi di Dottorato Chimica Organica nei suoi Aspetti Metodologici*** *New synthetic methods enabled by photochemistry and electrochemistry in flow*
10.45 - 11.00	**ORG OR140**	**Andrea Francesca Quivelli**	*Mild Approaches for Copper-Catalysed Coupling Reactions: Ligand-Free Ullmann-type C–N and C–O Bond Formation in Deep Eutectic Solvents*
11.00 - 11.15	**ORG OR141**	**Marco Rabuffetti**	*Stereoselective monoreduction of bulky 1,2-dicarbonyls catalyzed by a benzyl reductase from Pichia glucozyma (KRED1-Pglu)*
11.15 - 11.30	**ORG OR142**	**Daniele Ragno**	*Regiodivergent Isosorbide Acylation by Oxidative NHC-Catalysis in Batch and Continuous-Flow*
11.30 - 12.00	**Break**		
12.00 - 12.15	**ORG OR143**	**Giorgio Rizzo**	*Palladium anchored on Silk Fibroin as suitable catalyst for Suzuki-Miyaura Cross-Coupling Reactions*
12.15 - 12.30	**ORG OR144**	**Patrizio Russo**	*Novel Synthesis of Thienofuranone Derivates by Pd-Catalyzed Carbonylation Reaction*
12.30 - 12.45	**ORG OR145**	**Gabriele Lupidi**	*Vitamin B2 Promoted Tandem Nef-Henry Reactions for the synthesis of Symmetrical β-Nitro Alcohols from Nitroalkanes*

12.45 - 13.00	**ORG OR146**	**Ida Ziccarelli**	*Synthesis of Isobenzofuranones, Isochromenones and Thienopyranones by a Pd-Catalyzed Oxidative Carbonylation Approach*

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CHIMICA FARMACEUTICA (FAR)

- Orals
- Posters

Old but Gold: tracking the new guise of histone deacetylases as biomarkers and therapeutic targets in rare diseases. The role of isoform 6

Giuseppe Campiani

[a] *Department of Biotechnology, Chemistry and Pharmacy, University of Siena, IT*

Epigenetic regulation orchestrates many cellular processes and greatly influences key disease mechanisms. Histone deacetylase (HDAC) enzymes play a crucial role either as biomarkers or therapeutic targets owing to their involvement in specific pathophysiological pathways. The HDAC6 isoform, due to its unique cytoplasmic localization, modulates the acetylation status of tubulin, HSP90, TGF-β, and peroxiredoxins. HDAC6 also exerts noncatalytic activities through its interaction with ubiquitin. Both catalytic and noncatalytic functions of HDACs are being actively studied in the field of specific rare disorders beyond the well-established role in carcinogenesis. The application of HDACs inhibitors in rare diseases, such as *Idiopathic Pulmonary Fibrosis* (IPF), *Inherited Retinal disorders* (IRDs) such as *Retinitis Pigmentosa*, and *Rett Syndrome*, and an evolutionary strategy of specific structural features successfully applied in developing selective or dual acting inhibitors is outlined, highlighting the therapeutic potential of these innovative and targeted disease-modifying agents.

Millions of people worldwide suffer from lung diseases and, among them, interstitial lung diseases (ILDs) affect the lung interstitium where the pathological deposition of collagen and other connective tissue proteins causes progressive scarring and fibrosis. This disorganized damaged tissue strongly impairs the lungs functioning with devastating consequences in terms of functional capacity, quality of life, and increased mortality.[1] The most relevant ILDs may be associated with a progressive fibrosing phenotype and are classified as progressive-fibrosing rare diseases. The most common of these, characterized by a poor prognosis, is IPF. IPF was associated with aberrant HDAC activities [1] as confirmed by our immunohistochemistry studies on HDAC6 overexpression in IPF lung tissues. Blindness arising from retinal or macular degeneration results in significant social, health and economic burden. In IRDs, most patients have no access to an effective treatment. Although genetically and clinically distinct, macular and retinal degenerations share pathological hallmarks: photoreceptor degeneration, retinal pigment epithelium atrophy, oxidative stress, hypoxia and defective autophagy. Activation of HDACs in animal models of IRDs was documented. [2] We evaluated the potential of selective HDAC6 inhibitors to preserve retinal morphology or restore vision in zebrafish atp6v0e1$^{-/-}$ and mouse rd10 models. HDAC6i-treated atp6v0e1$^{-/-}$ zebrafish show marked improvement in vision. Proteomic profiling identified ubiquitin-proteasome, phototransduction, metabolism and phagosome as pathways whose altered expression correlated with HDACi-mediated restoration of vision. Mutations in MECP2 gene have been identified in >95% patients with Rett Syndrome. We investigated transcriptome changes in neurons differentiated from induced Pluripotent Stem Cells (iPSCs) derived from patients with different mutations. Profiling by RNA-seq in terminally differentiated neurons revealed a prominent GABAergic circuit disruption along with a perturbation of cytoskeleton dynamics. [3] In particular, in mutated neurons the significant decrease of acetylated α-tubulin could be reverted by treatment with our selective HDAC6is. These findings contribute to shed light on Rett pathogenic mechanisms and provide hints for the treatment of Rett-associated epileptic behavior as well as for the definition of new therapeutic strategies for Rett syndrome.

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The role of the secondary binding pocket in GPCR pharmacology

György M. Keserű

Medicinal Chemistry Research Group, Research Center for Natural Sciences, Hungary

G-protein coupled receptors (GPCRs) are considered important therapeutic targets due to their pathophysiological significance and pharmacological relevance. Endogenous ligands bind to the orthosteric binding pocket (OBP) embedded in the intrahelical space of the receptor. During the last years, however, it has been turned out that in many receptors there is secondary binding pocket (SBP) located in the extracellular vestibule that is much less conserved. In some cases it serves as a stable allosteric site harbouring allosteric ligands that modulate the pharmacology of orthosteric binders. In other cases it is used by bitopic compounds occupying both the OBP and SBP. In these terms, SBP binding moieties might influence the pharmacology of the bitopic ligands. Together with others, our research group showed that SBP binders contribute significantly to the affinity, selectivity, functional activity, functional selectivity and binding kinetics of bitopic ligands.

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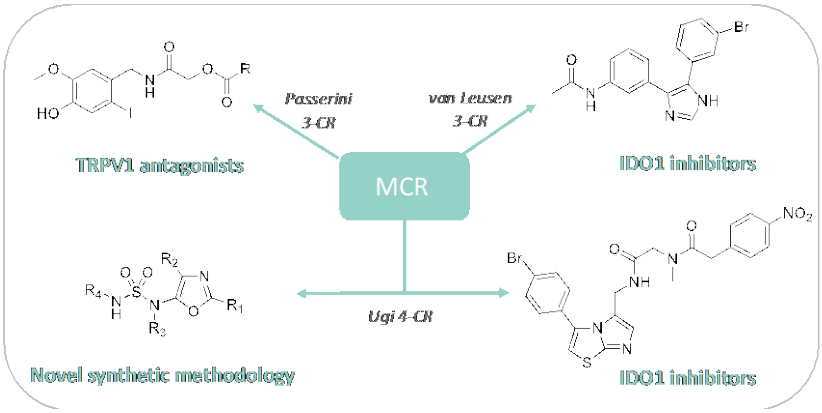
The power of multi-component reactions in drug discovery: soft drugs, PROTACs and more

Tracey Pirali

[a] *Department of Pharmaceutical Sciences, Università degli Studi del Piemonte Orientale, Via Bovio 6, 28100 Novara, Italy*

Chemists discover novel reactions every day: some of these transformations fall into oblivion, while others become part of the arsenal that is used to expand chemical space.
In the landscape of modern medicinal chemistry, multi-component reactions (MCRs) have definitely established themselves as sustainable, versatile and protecting group-free transformations.[1] They have amply demonstrated their usefulness in R&D, from the discovery of novel bioactive compounds to the scale-up of drugs, as exemplified by the well-known telaprevir.
Over the years, our group has capitalized on MCRs throughout different medicinal chemistry programs and in this communication some case studies, in which multicomponent chemistry, molecular modelling and biological need are closely intertwined, will be presented.
As an example, we have used the Passerini reaction to synthesize a library of topical soft capsaicinoids: thanks to the ester soft spot, they are hydrolyzed in plasma to inactive metabolites without exerting the systemic side-effects that have hampered the use of TRPV1 antagonists so far.[2] The low cost associated with the synthesis has allowed the launch of a soft capsaicinoid-based cosmetic product on the market.
The van Leusen[3] and the Ugi reaction[4] have been exploited in the discovery of inhibitors of indoleamine-2,3-dioxygenase 1 (IDO1), an enzyme that plays a pivotal role in cancer immune escape. These efforts have led to the serendipitous discovery of an unprecedented binding mode in the IDO1 active site[4] and of a novel synthetic methodology to access 5-sulfamido oxazoles.[5]
Finally, our very recent discovery of a cost-effective and reliable methodology based on Ugi and split-Ugi reactions[6] to synthesize Proteolysis Targeting Chimeras (PROTACs) will be disclosed.



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Navigating the antiviral drug discovery space: exploring different routes toward new broad-spectrum agents

Marco Radi

[a] *Dipartimento di Scienze degli Alimenti e del Farmaco, Università degli Studi di Parma, Parco Area delle Scienze, 27/A, 43124 Parma, Italy. Email: marco.radi@unipr.it*

Viral pathogens represent a major threat for the human population, sickening, disabling and killing millions of people worldwide each year. As human activity takes people into new environments or down to anti-scientific pathways, the risk of zoonotic virus spillover into humans increases and, along with that, the possibility of new epidemic outbreaks such as the SARS-CoV-2 pandemics. An additional problem is represented by coinfections, not only by different viruses in the same family, but also by different virus families, which creates immune response disorders, confusion in diagnosis and delays in treatment, leading to additive or synergistic morbidities. It is clear that vaccines alone are not enough to block the rising tide of emerging viral diseases and that successful containment of present and future epidemics of emerging viral agents, necessarily requires to be strongly supported by new antiviral drugs for an "early detection, early response" approach.

Unfortunately, the currently available antiviral arsenal is quite limited and only a few diseases caused by specific viruses (e.g. influenza, HIV, hepatitis C) can be treated with a simple pill. Therefore, the development of broad-spectrum antiviral agents (BSAAs) capable of inhibiting the replication of multiple viruses belonging to different families, is an ambitious but attractive option in preparedness for outbreaks of previously unknown viral diseases and also for the treatment of widespread viral infections and coinfections where an effective drug is not available yet.

In this presentation I will discuss different approaches (host-targeting, guest-targeting, multi-targeting) recently pursued by our research group for the discovery of new BSAAs able to inhibit the replication of different viruses at low micromolar and sub-micromolar concentrations.

Leveraging precision electrophile signaling toward drug discovery

Yimon Aye and her team members

[a] *Swiss Federal Institute of Technology (EPFL), Lausanne, Switzerland*

Precisely timed and spatially regulated electrophilic chemical signals are slowly being implicated as bona fide signaling events in numerous cells[1]. However, modeling these low-stoichiometry signaling events and defining the precise biological impacts of localized signals under physiologic conditions has proven to be highly challenging. The first half of the presentation will spotlight a unique set of proximity-directed chemical biology tools that enables interrogation into functional consequences of specific redox-linked events: namely, T-REX™ precision electrophile delivery and G-REX™ electrophile-ligandability profiling in living systems, and how using these technologies have enabled us to identify bona fide "*first responders*" that interact with native signaling electrophiles under close to endogenous redox signaling conditions (i.e., "k_{cat}/K_m"-like)[2]. Our data show that these first responders lie at nexuses between electrophile- and canonical-signaling pathways. Thus, these proteins translate information encoded by electrophiles to phosphate or ubiquitin to reroute signaling pathway flux, even at the organismal level. The second half of the presentation will relate to our latest data of unique relevance to medicinal chemistry research: i.e., our new ability to discover and functionally decipher precision electrophile signaling mechanisms toward targeted therapeutics and novel target discovery. Here, I will discuss successful small-molecule targeting of otherwise hard-to-treat *pten*-null triple-negative breast cancers in cells and xenograft mouse tumor models, guided by our recent identification of protein-isoform-specific native electrophilic metabolite sensing in living cells and larval zebrafish.

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Enabling synthesis and technologies to develop bile acid-inspired lead compounds

Antimo Gioiello

Department of Pharmaceutical Sciences, University of Perugia, Italy.

Since the end-1990s bile acids and their receptors have become increasingly important targets in drug discovery research for the management of a variety of liver and potentially other diseases.[1] The field was in fact relatively dormant until the discovery that bile acids were the endogenous ligands of what was then an orphan nuclear receptor known as FXR. At that time bile acids and receptor targets began to be ascribed physiological functions that went beyond their traditional role in cholesterol homeostasis and digestion of fats and fat-soluble vitamins, ushering in a renaissance for bile acids and their therapeutic potential.[2]
Unquestionably, an important challenge for bile acid drug discovery relies in the design and realization of methodologies that enable the synthetic accessibility of poorly reactive, unexplored and sterically hidden positions of the steroidal scaffold. Not less important, synthesis routes to prepare bile acid leads and clinical candidates must guarantee an easy scalability, a high efficiency in terms of yield, step-economy and cost, and they must satisfy sustainability and safety criteria.
In this talk, case studies related with the discovery, synthesis design and optimization of novel bile acids as a wealthy source of chemical leads and probes are reported and discussed. Particular emphasis will be devoted to the mechanistic aspects and the technological solutions that have aided to address synthetic limitations and streamline the development of selected lead compounds.

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The selective inhibition of histone deacetylase 6 (HDAC6)

Andrea Stevenazzi

R&D, Italfarmaco Group, Via dei Lavoratori 54, I-20092 Cinisello Balsamo, Milan, Italy

HDAC6 is an emerging drug target correlated to a variety of pathologies such as autoimmune disorders, neurodegenerative diseases, and cancer.[1] Of note, the selective inhibition of this enzyme does not show cytotoxic effects normally associated with the inhibition of Class I HDAC isoforms.[2] The discovery in 2010 of Tubastatin A,[3] one of the first druglike inhibitors of HDAC6, and the publication in 2016 of the crystal structures of a range of inhibitors bound to the catalytic domain 2 (CD2) of zebrafish HDAC6[4,5] boosted the search for new generations of selective inhibitors.
With the aim of improving the stability of internally developed selective inhibitors, the identification of a new class of benzohydroxamate-based HDAC6 inhibitors was successfully achieved via Scaffold Hopping.[6]

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Addressing underexplored anti-infective targets

Anna K. H. Hirsch

Department of Drug Design and Optimization, Helmholtz Institute for Pharmaceutical Research Saarland (HIPS), Helmholtz Centre for Infection Research & Department of Pharmacy, Saarland University, 66123 Saarbrücken, Germany

The challenges associated with anti-infective drug-discovery programmes can be tackled by combining phenotypic antibacterial screening with several established and unprecedented hit-identification strategies. This approach will be illustrated using two targets: The first is a vitamin transporter from the energy-coupling factor (ECF) class, which consist of an energising module and a substrate-binding protein (S-component). Different S-components can interact with the same energising module. Here, we report on the structure-based virtual screening (SBVS), design, synthesis and structure–activity relationships (SARs) of the first class of selective, antibacterial agents against the energy-coupling factor (ECF) transporters. Having identified a druggable pocket in the crystal structure of the *L. delbrueckii* ECF transporter, which should play a key role in the unique mechanism of transport, our SBVS of the zinc library afforded a fragment-like hit with good in vitro and cell-based activity and a good in vitro ADMET profile. Having established a new cell-based uptake assay in *Lactobacillus casei*, we identified a low-micromolar inhibitor of the ECF transporters with a broad spectrum of activity (MIC values in the single-digit micromolar range) and a lack of resistance development.
The second is an extracellular metalloprotease and virulence factor of *Pseudomonas aeruginosa*, the elastase LasB. In a structure-based manner we succeeded in optimising highly selective and potent inhibitors as promising anti-virulence agents. Multiparameter optimisation is currently ongoing based on extensive *in vitro* and *ex vivo* profiling, including the establishment of complex biological assays.

Targeting protein-protein interactions involved in oxidative stress using fragment-based drug discovery

Anders Bach[a]

[a] *Department of Drug Design and Pharmacology, Faculty of Health and Medical Sciences, University of Copenhagen, DK-2100 Copenhagen, Denmark.*

Oxidative stress plays a crucial role in numerous diseases and pathological processes such as inflammation and neurotoxicity. To generate new chemical probes and potential drug leads we target protein-protein interactions involved in oxidative stress by using fragment-based drug discovery (FBDD). We focus on the superoxide-generating multi-subunit enzyme complex NADPH oxidase 2 (NOX2) and the adaptor protein Keap1, which regulates the endogenous antioxidant response.

NOX2 has great potential as a therapeutic target against several diseases. However, developing druglike, specific, and reliable NOX2 inhibitors has been very difficult. By using FBDD we have made a unique series of dimeric NOX2 inhibitors exhibiting a novel mechanism of action [1]. By binding to p47phox, these compounds block the interaction with the p22phox subunit (K_i < 0.5 μM) and prevent assembling and activation of the NOX2 complex, which leads to reduced levels of superoxide in cells. Optimization is ongoing with the aim of conducting proof-of-principle pharmacological *in vivo* studies.

Keap1 is an adaptor protein of Cullin3-based ubiquitin E3 ligase and serves as an oxidative stress sensor. We have addressed this target by several means: Initially, we did a comparative assessment study of all known Keap1 inhibitors and found that only about half of the published compounds were genuine Keap1 binders, while the rest seemed to be various types of false positives [2]. We then deconstructed the known compounds into a target-biased library of 77 fragments and tested them for Keap1 binding using four orthogonal biophysical assays. The binding modes of key fragment hits where determined by X-ray crystallography, which allowed us to merge two fragments into novel compounds with high affinities to Keap1 [3]. We have also screened and validated 2,500 commercially available fragments using the same four assays, which led to 28 high-priority hits and 13 fragment-Keap1 costructures, which are currently guiding our optimization process. Recently, we screened Diamond Light Source's 768 XChem fragments by X-ray crystallography, and found 80 novel fragment hits binding in the active site of Keap1, which are also subject to chemical optimization.

In this presentation, I will summarize our efforts in targeting NOX2 and Keap1 by FBDD and show our very latest results.

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Chemical and molecular mechanisms of cellular and extra-cellular antioxidants

Giancarlo Aldini

Department of Pharmaceutical Sciences, Università degli Studi di Milano, Milan, Italy

Oxidative stress is defined as an excess production of reactive oxygen species (ROS) relative to antioxidants. Oxidative stress plays a central role in the pathogenesis of various chronic inflammatory disorders including diabetic complications, cardiovascular disease, aging, neurodegenerative disease, autoimmune disorders, and pulmonary fibrosis [1].
Based on its pathogenetic role, oxidative stress is a drug target which needs to be modulated in order to reach preventive/therapeutic strategies. To date, several natural and synthetic molecules have been designed as antioxidant agents, mainly acting through radical-scavenging, H-transferring or electron donor mechanisms. However, from a thermodynamic and kinetic point of view, it has been recognized that most of the molecules designed to act as radical scavenger in in vitro conditions do not reduce oxidative stress in cells through this mechanism. Most of the molecules acting as in vivo antioxidants are converted through an oxidative reaction to the reactive electrophilic metabolites which activate the Nrf2-Keap1 pathway resulting in an increase in the antioxidant enzymes and their substrates, glutathione, thioredoxin and NADPH [2]. Hence, many antioxidants do not reduce oxidative stress in in vivo conditions by a direct radical scavenging mechanism but indirectly, through Nrf2 signalling. Many natural dietary components act through such a mechanism such as carotenoids, curcumin and polyphenols. In particular, among dietary polyphenols, procyanidins are recognized as effective in vivo antioxidants. They are metabolized to 5-(4'-hydroxyphenyl)-gamma-valerolactone by gut microbiota, which is absorbed and when present in an oxidant milieu is oxidized to the corresponding quinone able to react with the thiol groups of Keap1 thus activating the Nrf2 translocation. [3]

The antioxidant defense mechanism at extracellular level is quite different since it is not mediated by enzymatic antioxidants which are contained in a negligible amount in respect to their content in cells. Albumin is the main extracellular antioxidant due to the reactivity (acidity) of Cys34 which represents the most abundant antioxidant thiol. Oxidation of Cys34 leads to the corresponding sulfenic derivative which then reacts with Cys forming cysteinylated albumin and this reaction prevents the irreversible oxidation of the thiol to sulfinic and sulfonic acid derivatives. We found that compounds able to regenerate Cys34 from the cysteinylated isoform through a disulfide breaking mechanism, greatly improve the antioxidant plasma capacity. The well-known antioxidant agent N-acetylcysteine (NAC) acts through this mechanism. In both in vitro and ex-vivo conditions NAC dose-dependently restores mercaptoalbumin from the cysteinylated form as measured by MS and increases the antioxidant plasma potential as measured by the ORAC assay [4].

In conclusion the molecular mechanism through which natural and synthetic molecules act in in vivo conditions need to be revised. A direct radical scavenging mechanim is effective for some specific compounds such as vitamin E but for most of natural and synthetic compounds, an indirect effect based on Nrf2 activation (cell compartment) and on disulfide breaking (extracellular compartment) should be considered and taken into account for a rational drug design.

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Discovery of a picomolar potency corrector of F508del-CFTR chloride channel

Tiziano Bandiera[a]; Fabio Bertozzi[a]; Federico Sorana[a]; Francesco Berti[a]; Alejandra Rodríguez-Gimeno[a]; Sine Mandrup Bertozzi[b]; Giuliana Ottonello[b]; Andrea Armirotti[b]; Raffaele Spanò[b]; Rosalia Bertorelli[b]; Ilaria Penna[a]; Debora Russo[a]; Emanuela Caci[c]; Loretta Ferrera[c]; Valeria Tomati[c]; Elvira Sondo[c]; Ambra Gianotti[c]; Emanuela Pesce[c]; Paolo Scudieri[d]; Nicoletta Pedemonte[c]; Luis J.V. Galietta[d,e]

[a] *D3-PharmaChemistry, Istituto Italiano di Tecnologia (IIT), Genova, Italy;* [b] *Analytical Chemistry and Translational Pharmacology, Istituto Italiano di Tecnologia (IIT), Genova, Italy;* [c] *U.O.C. Genetica Medica, Istituto Giannina Gaslini (IGG), Genova, Italy;* [d] *Telethon Institute of Genetics and Medicine (TIGEM), Pozzuoli (Napoli), Italy;* [e] *Department of Translational Medical Sciences (DISMET), University of Naples Federico II, Naples, Italy.*

The deletion of phenylalanine at position 508 (F508del) of the CFTR protein is the most frequent mutation in patients with cystic fibrosis (CF). This mutation causes a severe defect in protein folding and stability, and impairs the gating behavior. The folding and stability defect can be treated with compounds known as correctors, whereas the gating defect can be overcome by compounds called potentiators [1, 2]. The first two correctors approved for the treatment of CF patients bearing the F508del-CFTR mutation, i.e., lumacaftor (VX-809) and tezacaftor (VX-661), given in combination with the potentiator ivacaftor (VX-770), showed limited therapeutic benefit. The recently approved combination of a new corrector, elexacaftor (VX-445), with tezacaftor and ivacaftor shows much better efficacy [3]. This notwithstanding, the need for new and highly effective correctors remains.

To discover new correctors, we conducted a phenotypic screening of a collection of about 15,000 commercial compounds, using FRT and CFBE41o- cells stably expressing F508del-CFTR and the Halide-Sensitive Yellow Fluorescent Protein (HS-YFP) [4]. Two compounds were identified as hits in both cell types. The hits, belonging to different chemical classes, were subjected to rounds of chemical modifications, and functional evaluation in different assays, to derive information on the structure-activity relationship for each chemical class.

One of the two classes was investigated more extensively, leading to compounds with high potency and efficacy in rescuing the activity of F508del-CFTR in human bronchial epithelial (HBE) cells from CF patients homozygous for the F508del mutation.

This work led to ARN23765, a corrector with EC_{50} of 38 picomolar in HBE cells and showing high efficacy and synergy with other types of correctors [5]. The compound has been extensively characterized for its drug-like properties and is currently a candidate for preclinical development.

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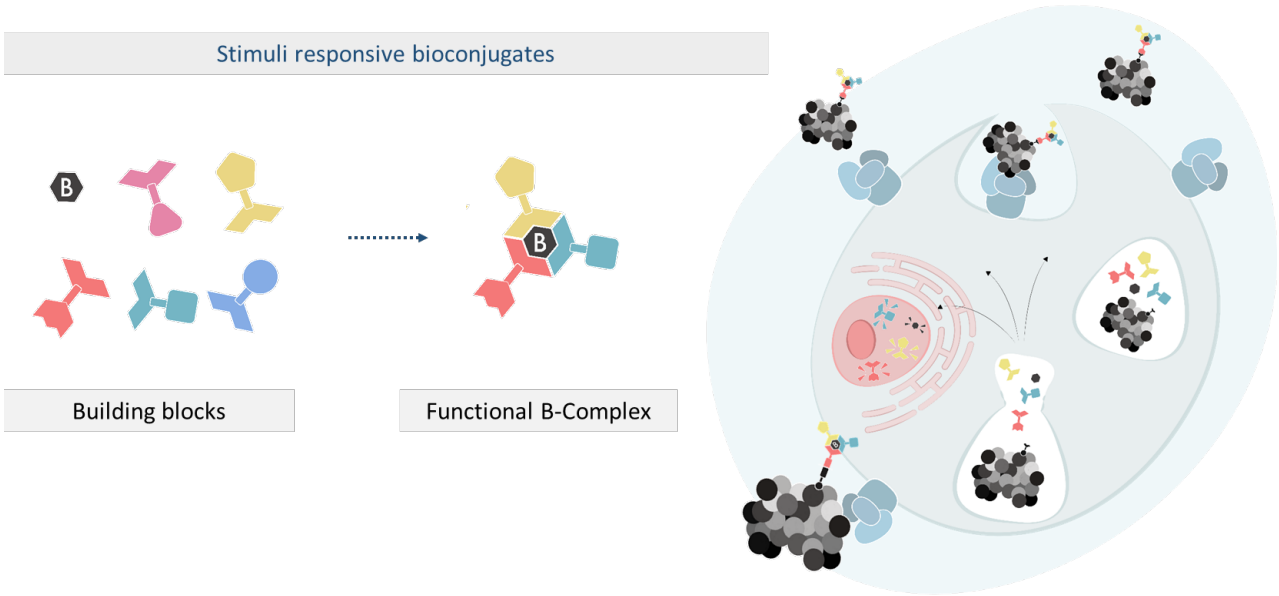
Exploring B-complexes as likers for targeting drug conjugates

Pedro M. P. Gois

Research Institute for Medicines (iMed.ULisboa) Pharmacy Faculty, Universidade de Lisboa

Targeting drug conjugates, emerged as a powerful class of chemotherapeutic agents that are capable of sparing healthy tissues by liberating the cytotoxic payload upon specific antigen recognition. A considerable body of work in this field highlighted that targeting drug conjugates therapeutic efficacy, correlates well with the conjugate homogeneity and activation of the drug at the diseased site. Therefore, the linker technology used to connect both functions contributes decisively to the therapeutic usefulness of these constructs. In this communication will be presented our most recent finding on the design of functional likers for targeting drug conjugates, based on boron complexes (B-complexes)[1] that can be modulated to exhibit fluorescence and to respond to glutathione, pH or reactive oxygen species stimulus.[2-4]



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Design and Therapeutic Potential of Adenosine and P2Y Receptor Ligands

Kenneth A. Jacobson[a]

[a] *National Institute of Diabetes & Digestive & Kidney Diseases, National Institutes of Health, Bethesda, Maryland, USA.*

The purinergic signaling system responds to extracellular nucleosides and mono- and dinucleotides. Purinergic G protein-coupled receptors (GPCRs) include four adenosine receptors and eight P2Y receptors. Every cell in the body has some combination of purinergic receptors, which are relevant to many diseases. Four themes will be presented: Structural probing of adenosine and P2Y receptors enable ligand discovery and reveal activation mechanisms; Conformational control of GPCR ligand specificity [1]; Tethered drugs, fluorescent probes and nanoconjugates; Light-directed biochemistry. With X-ray or cryo-EM structures now available for a few receptors, we use computational modeling methods to guide ligand design. We introduced the first A_3 adenosine agonists, which are better tolerated systemically than agonists of other subtypes, and two of which are now in advanced clinical trials for psoriasis, liver cancer, non-alcoholic steatohepatitis, with no serious adverse effects in >2000 human subjects. A structure-based approach, using the (N)-methanocarba modification of the ribose moiety and other has been taken to enhance the selectivity of A_3 agonists to >10,000-fold, and to demonstrate utility in chronic pain models [2]. P2Y receptors boost the immune response, and therefore antagonists, such as $P2Y_{14}$, are being designed as treatment for inflammatory and allergic conditions [3].

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Lecture for the receipt of the "Giordano Giacomello" medal by the Medicinal Chemistry Division of the Italian Chemical Society

Antonello Mai

[a] *Department of Drug Chemistry and Technologies, Sapienza University of Rome, P.le Aldo Moro 5, 00185 Roma, Italy*

I am very grateful to the Division of Medicinal Chemistry for the award of the "Giordano Giacomello" medal. In my talk I will retrace the salient features of my scientific career, focusing mainly on the following topics:
1 - design and synthesis of non-nucleoside inhibitors of HIV-1 reverse transcriptase with pyrimidin-4(3*H*)-one structure. Such compounds after extensive med chem studies showed subnanomolar potency against wt HIV-1 and submicromolar EC_{50} values against HIV-1 clinical isolates and mutant strains.
2 - design and synthesis of HDAC inhibitors for the treatment of cancer diseases. With this research we were able to identify pan- as well as class- and isoform-selective HDAC inhibitors. Such last compounds was used by many scientists to dissect the role(s) of single class/isoform of HDAC in diverse physio-pathological contexts.
3 – focusing on other epigenetic targets, we described inhibitors and activators of sirtuins, and inhibitors of HATs, HKMTs and PRMTs, KDMs (both LSD1 and Jmj-C enzymes), DNMTs, studying their biological effects in cancer and non-cancer (metabolism, central nervous system, microbial and parasitic infections) diseases.
4 - recently we have turned our efforts to epi-polypharmacology, with the design and synthesis of dual/multitarget agents hitting at least one epigenetic target, to better treat complex, multi-factorial diseases.

Targeting prostate cancer with multiple-targeting ligands: activity on both AKR1C3 enzyme and androgen receptor

Pippione, A.C.;[a] Kurt, Z.;[b] Sainas, S.;[a] Rolando, B.;[a] Kovachka, S.;[a] Spyrakis, F.;[a] Buschini, A.;[c] Montalbano, S.;[c] Oliaro Bosso, S.;[a] Boschi, D.[a] and Lolli. M.L.[a]

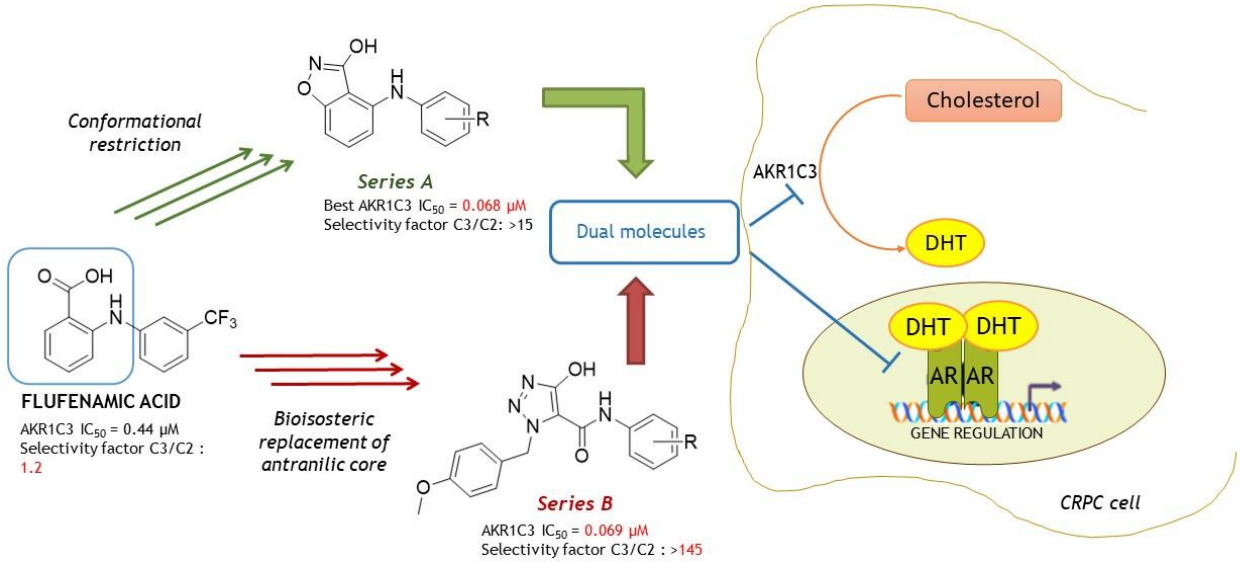
[a] University of Torino, Dept of Science and Drug Technology, via Pietro Giuria 9, Torino, Italy; [b] Ankara University, Faculty of Pharmacy, Dept of Pharmaceutical Chemistry, Ankara, Turkey; [c] University of Parma, Dept of Chemistry, Life and Env. Sust. Sciences, Parco Area delle Scienze 11/a, Parma, Italy

The enzyme aldo-keto reductase 1C3 (AKR1C3) plays a vital role in the biosynthesis of androgens (testosterone and DHT) in prostate and is considered an attractive target in Castration Resistant Prostate Cancer (CRPC).[1] At the same time, antagonists to Androgen Receptor (AR) as enzalutamide and darolutamide are used as anticancer drugs in CRPC patients. The two targets are compatible in terms of ligand accommodation as they are both able to interact with DHT as product and ligand, respectively.

Our group already discovered new potent and selective AKR1C3 inhibitors, designed though a scaffold hopping approach applied to flufenamic acid (FLU, Figure 1).[1,2] We here propose new derivatives for both the benzoisoxazole and the hydroxytriazole series, and move our attention on obtaining multiple ligands for both AKR1C3 and AR.

To do this, we identified structural elements required for activity on AR and found some AKR1C3 inhibitors able to play AR antagonism activity; this represent a starting point for multiple-targeting ligand development applied to CRPC. The potency and dual action of new compounds are translated into citotoxicity against CRPC cellular models.

In silico design, synthesis and biological activity on AKR1C3 enzyme of new compounds, as well as their capability to address AR, are here described.



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Synthesis and characterization of new A_3 adenosine receptors ligands as potential anti-cancer agents

Spinaci A., Buccioni M., Dal Ben D., Lambertucci C., Marucci G., Santoni G., Volpini R.

School of Pharmacy, Medicinal Chemistry Unit, University of Camerino, via S. Agostino 1, 62032 Camerino (MC), Italy.

andrea.spinaci@unicam.it

The A_3 adenosine receptors (ARs) are involved in different cytoprotective actions and their ligands are reported to be endowed with anti-inflammatory, anti-tumor, and cardioprotective actions. Numerous studies also reported how this receptor subtype is important in the proliferation cells process and, consequentially, how it could play a key role in the treatment of cancer. In a recent work [1], the N^6-(2,2-diphenylethyl)-2-hexynyladenosine and the N^6-(2-phenylethyl)-2-(2-phenylethylamino)adenosine were found to possess cytotoxic activity on human prostate cancer cells (PC3), on Hepatocellular carcinoma cells (Hep G2) and colorectal carcinoma epithelial cells (Caco-2) comparable to 2-chloro-N^6-iodobenzyl-4'-*N*-methylcarboxamidoadenosine (Cl-IBMECA), an A_3AR agonist presently in clinical trials for hepatocellular carcinoma. On this basis, a new series disubstituted adenosine derivatives bearing different alkynyl/thioalkyl/aminoalkyl chains in 2-position combined with a 2,2-diphenylethyl and 2-phenylethyl substituents in N^6-position have been synthesized. The desired nucleosides were obtained using a divergent approach starting from commercial guanosine which was modified in order to obtain the versatile intermediates 6-chloro-2-iodo-purine riboside. Reaction of this intermediate with 2,2-diphenylethylamine or 2-phenylethylamine gave the 2-iodo-N^6-substituted derivative which were treated with the suitable alkynes, amines, and thiols in order to obtain the desired compounds. Binding studies at human ARs stably transfected in Chinese hamster ovary cells demonstrated that all the new substituted nucleosides show good affinity and different degree of selectivity for the A_3ARs. The antiproliferative effect of them and 2-Cl-IB-MECA, used as reference, were evaluated in PC3 cell line by the sulphorhodamine B (SRB) assay, according to the National Cancer Institute protocol [2]. All the compounds demonstrated to reduce dose-dependently the growth after 48 h of culture. The antitumor activity was estimated by measurements of three parameters: Growth Inhibition 50 (GI_{50}), the drug concentration (μM) required to inhibit 50% net of cell growth; Total Growth Inhibition (TGI), the drug concentration (μM) required to inhibit 100% of cell growth; Lethal Concentration 50 (LC_{50}), the drug concentration (μM) required to kill 50% of the initial cell number. The results demonstrated that the N^6-(2-phenylethyl)-2-(2-phenylethynyl)adenosine and the N^6-(2,2-diphenylethyl)-2-(2-phenylethynyl)adenosine showed higher activity than Cl-IBMECA in all the three experiments.

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Design, synthesis, and biological evaluation of a new series of pyrazolo[3,4-*d*]pyrimidines active as SGK1 inhibitors. A lead optimization study

F. Musumeci,[a] *L. D'Antona,*[b] *A. Carbone,*[a] *F. Ortuso,*[b] *S. Alcaro,*[b] *N. Perrotti,*[b] *S. Schenone*[a]

[a]*Department of Pharmacy, University of Genoa, Viale Benedetto XV, 3, 16132 Genoa, Italy;* [b]*Department of "Scienze della Salute", University "Magna Graecia" of Catanzaro, Viale Europa, 88100 Catanzaro, Italy*

SGK1 (serum- and glucocorticoid-regulated kinase) is a serine-threonine kinase which is involved in different diseases including cancer and metabolic syndrome. Despite the critical role of this kinase in the development and resistance of human tumors, only a small number of SGK1 inhibitors are reported in the literature so far.[1]

Among our library of pyrazolo[3,4-*d*]pyrimidines active as Src/Abl inhibitors, we identified SI113 (**Figure 1**) as a quite potent and selective SGK1 inhibitor (IC_{50} = 600 nM, selectivity almost 100-fold higher compared to the analog kinase Akt1).[2] SI113 is active *in vitro* in several cancer cell lines overexpressing SGK1, and *in vivo* in xenograft models of human hepatocellular carcinoma, and ovarian cancer. Furthermore, SI113 shows synergistic effects with radiotherapy and classical antitumor agents.[3,4]

Based on these encouraging results, we started a lead optimization study aimed at identifying new SGK1 inhibitors endowed with higher potency and good pharmacokinetic properties. A virtual library of compounds of feasible synthesis was designed and submitted to molecular modeling studies. The *in silico* most promising compounds and a set of derivatives designed to extend the structure-activity relationship evaluation were synthesized (compounds **1a-z**, **Figure 1**). Then, the activity of the new derivatives towards SGK1 and the A2780 ovarian cancer cell line was evaluated. Interestingly, two compounds showed a better activity profile than SI113 on cells. Formulation and *in vivo* studies on the most active derivatives are ongoing. Biological results will be discussed.

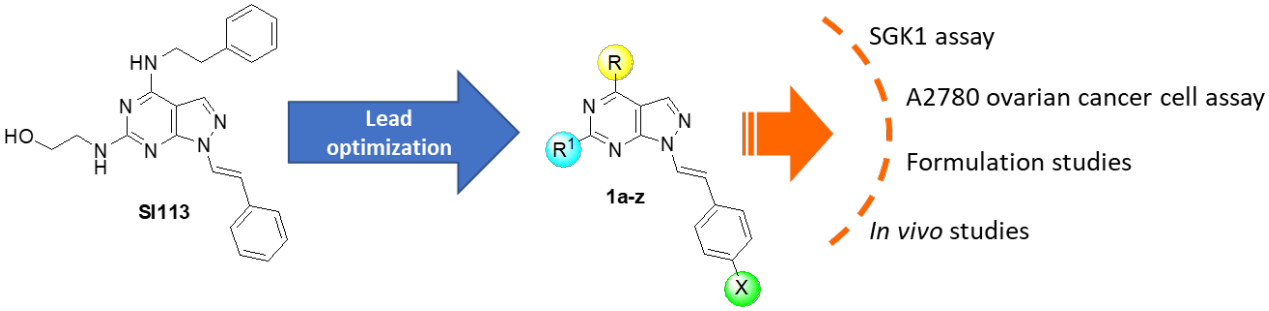

Figure 1. Structure of SI113 and schematic representation of the lead optimization study.

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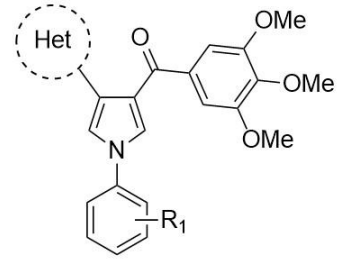
New pyrroles derivatives as anti-glioblastoma and anti-chronic myeloid leukemia agents

*Michela Puxeddu,[a] Jessica Sebastiani,[a] Antonio Coluccia,[a] Marianna Bufano,[a] Ernest Hamel,[b] Te Liu,[c] Romano Silvestri,[a] Giuseppe La Regina[a,]**

[a]Laboratory affiliated with the Institute Pasteur Italy – Cenci Bolognetti Foundation, Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza Università di Roma, Piazzale Aldo Moro 5, 00185, Rome, Italy; [b]Frederick National Laboratory for Cancer Research, National Cancer Institute, National Institutes of Health, Frederick, Maryland 21702, United States; [c]Shanghai Geriatric Institute of Chinese Medicine, Shanghai University of Traditional Chinese Medicine, 365 South Xiangyang Road, Shanghai, China, 200031.
**giuseppe.laregina@uniroma1.it*

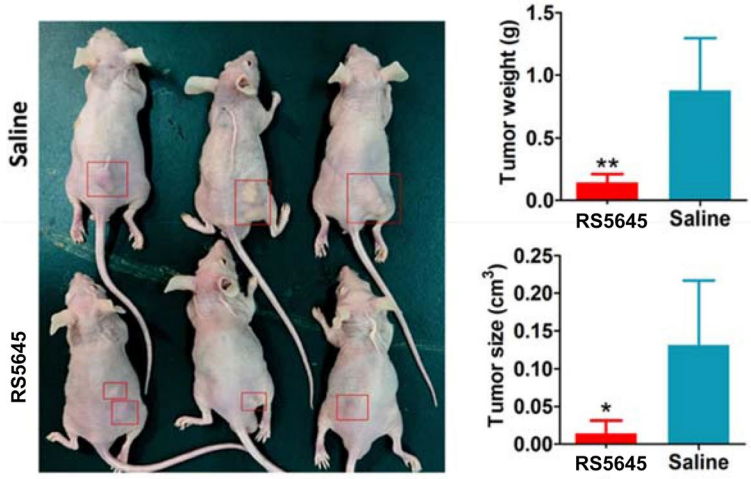
Long-term survivors of glioblastoma multiforme (GBM) are at high risk of developing second primary neoplasms, including leukemia. For these patients, the use of classic tyrosine kinase inhibitors (TKIs), such as imatinib mesylate, is strongly discouraged, since this treatment causes a tremendous increase of tumour and stem cell migration and invasion. We aimed to develop agents useful for the treatment of patients with GBM and chronic myeloid leukemia (CML) using an alternative mechanism of action from the TKIs, specifically based on the inhibition of tubulin polymerization (Chart 1).[1,2] (4-(Thiophen-3-yl)-1-(*p*-tolyl)-1*H*-pyrrol-3-yl)(3,4,5-trimethoxyphenyl)methanone (RS5645) and (1-(4-fluorophenyl)-4-(pyridin-4-yl)-1*H*-pyrrol-3-yl)(3,4,5-trimethoxyphenyl)methanone (RS5893) derivatives, as planned, not only inhibited tubulin polymerization, but also inhibited the proliferation of both GMB and CML cells, including those expressing the T315I mutation, at nanomolar concentrations. In *in vivo* experiments in BALB/cnu/nu mice injected subcutaneously with U87MG GBM cells, RS5645 significantly inhibited tumour growth, tumorigenesis and angiogenesis (Figure 1).

Chart 1. Chemical structure of new pyrrole derivatives.



24 New Compounds
R_1 = 3-Me, 4-Me, 4-F; Het = five or six member heterocycle.

Figure 1. *In vivo* tumorigenicity inhibition by new pyrrole derivatives of U87MG GBM cells.



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[2] This research was supported by Istituto Pasteur Italia – Fondazione Cenci Bolognetti (Call 2019, G.L.R.).

Identification and characterization of a potent TRPM8 antagonists with in vivo analgesic properties

Musella S.,[a] Bertamino A.,[b] Ostacolo C.,[c] Medina A.,[d] Di Sarno V.,[b] Lauro G.,[b] Ciaglia T.,[b] Pepe G.,[b] Basilicata M. G.,[b] Cristiano C.,[c] Gonzalez-Rodriguez S.,[d] Fernandez-Carvajal A.,[d] Bifulco G.,[b] Russo R.,[c] Gomez-Monterrey I.,[c] Campiglia P.[a,b]

[a] European Biomedical Research Institute (EBRIS); [b] Department of Pharmacy, University of Salerno; [c]Department of Pharmacy, University Federico II of Naples; [d]IDiBE, Universitas Miguel Hernández of Elche

Transient receptor potential melastatin type 8 (TRPM8) channel is a transmembrane Ca^{2+}-permeable nonselective cation channel activated by innocuous cool to cold temperatures (10−28 °C) and sensitive to voltage, phosphatidylinositol-4,5-biphosphate (PIP2), and different synthetic molecules. involved in a wide range of physiological and pathophysiological processes. In the last years, a correlation between TRPM8 overexpression in sensory neurons and neuropathic pain has been revealed particularly. For these reasons, the design of TRPM8 antagonists became an attractive strategy for neuropatic pain pharmacological treatments.[1,2] Our research group has been deeply involved in the development of TRPM8 modulators,[1-4] leading to the characterization of a tryptophan derivative, identified as the most potent (IC_{50} 0.2 ± 0.2 nM) and selective TRPM8 in-vitro antagonist whereas metabolically unstable.[3] Starting from the collected evidences and taking advantage of the recently released cryo-EM structure of the antagonist-bound TRPM8[5] we have performed in-silico studies to generate a homology model of the channel, leading to the identification of a putative binding site for the previously synthesized derivatives. The proposed binding site and antagonists binding mode were than used for the rational design of a small library of β-carboline-based antagonists aimed in maintaining the potency and the selectivity of the homologues, while improving metabolic stability. Synthesis of the designed compounds also led to the exploration and characterization of a new chemical pathway for the synthesis of indol-fused aminoacetales.[6] The compounds were characterized in-vitro for their TRPM8 antagonist activity by mean of calcium fluorimetric assays and patch clamp measurements. The most potent compound (**31a**, IC50 4.10 ± 1.2 nM), also showed subtype selectivity and metabolic stability, when challenged in vitro using liver microsomes. Thus, compound **31a** was also assayed in vivo showing significant target coverage in an icilin-induced WDS assay and in oxaliplatin-induced cold allodynia and CCI-induced thermal hyperalgesia mice models. These results demonstrate the efficacy of the TRPM8 agonists in animal models of injury-induced neuropathic pain also confirming the suitability of the β-carboline nucleus in the design of potent TRPM8 modulators, adding one more piece to the puzzle that composes the TRPM8 complex biology in the transmission and modulation of pain.

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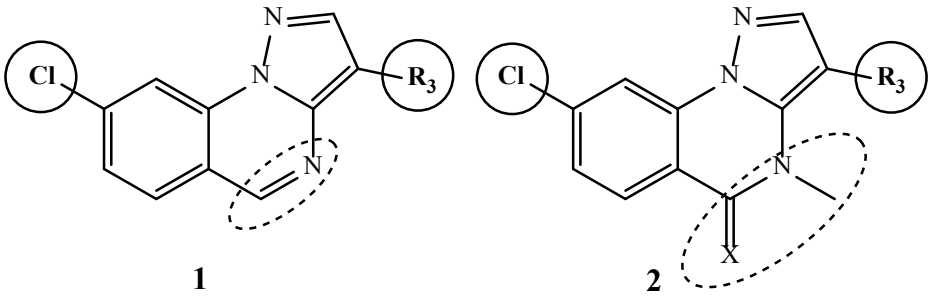
Synthesis of pyrazolo[1,5-a]quinazolines as ligand of α1β3γ2-GABAA receptor subtype and molecular modelling studies

Letizia Crocetti[a], Fabrizio Melani[a] and Maria Paola Mascia[b]

[a] Neurofarba, Pharmaceutical and Nutraceutical Section, University of Florence, Via Ugo Schiff 6, 50019, Sesto Fiorentino, Italy; [b]CNR – Institute of Neuroscience, Cittadella Unversitaria, Cagliari, Italy

The GABAAR is a receptor channel permeable to chloride ions, assembled in a pentameric structure[1]. It is formed by the combination of five subunits belonging to 8 families (α, β, γ, δ, ε, θ, ρ, π) and the most represented subtype in the CNS is the 2α12β2γ2-GABAAR[2]. In addition to the orthosteric site for the endogenous neurotransmitter GABA, many others binding sites for allosteric modulators are recognized in the GABAAR. The allosteric site of the benzodiazepine (BZR) is located at the interface of the α-γ subunits and it is also modulated by other ligands belonging to different chemical families[3]. The ligands can modulate GABAAR positively (PAMs) negatively (NAMs) or be silent (SAMs) and the pharmacological effects of benzodiazepines are influenced by the type of the α subunit present in the receptor (α1 sedative-hypnotic, amnesic, anticonvulsant effect; α2/α3 anxiolytic and muscle relaxant; α5 mnemonic processes)[4].
Our researches in the field of benzodiazepine receptor ligands afforded new 8-chloropyrazole[1,5-a]quinazoline (PQ) derivatives differently substituted at position 3 (structure 1). The PQ scaffold, as in lactamic (X = O) and in dihydro form (X = H, H) (structure 2), was also methylated at position 4, analogously to BZR high affinity ligands reported in the literature. All the synthesized compounds were used for the construction of a predictive model of molecular dynamics and statistical evaluation[5], in order to classify these new compounds as BZR agonists or antagonists. Moreover, the new compounds have been evaluated through electrophysiological studies on α1β2γ2L recombinant GABAA receptors of the *Xenopus laevis* oocytes, to evaluate their efficacy and confirm whether or not the goodness of the results of molecular dynamics.



1 **2**

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Discovery of CP86, a potent neuronal Kv7 channel activator with in vivo anticonvulsant effects

Ostacolo C.,[a] Iraci N.,[b,c] Miceli F.,[d] Bertamino A.,[e] Ciaglia T.,[e] Nappi P.,[d] Carotenuto L.,[d] Baroli G.,[d] Gomez-Monterrey I.M.,[a] Pepe G.,[e] Sommella E.M.,[e] Manfra M.,[c] Taglialatela M.,[d] Campiglia P.[e]

[a] Department of Pharmacy, University Federico II of Naples; [b] Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina [c] Department of Science, University of Basilicata [d] Department of Neuroscience, Reproductive Sciences and Dentistry, University Federico II of Naples; [e] Department of Pharmacy, University of Salerno

Kv7 K^+ channels play a pivotal role in controlling neuronal excitability, representing attractive pharmacological targets for the treatment of different neurological disorders, including epilepsy. In fact, the Kv7.2/7.3 agonist retigabine has been approved in 2011 as add-on treatment for adults with drug-resistant partial onset seizures with or without secondary generalisation. However, due to several drawbacks and side effects, the clinical use of retigabine has been declining over the years, leading to its discontinuation in 2017.[1] In the attempt to overcome some of these limitations we started from our previously published results[1] to perform in-silico studies of the retigabine binding site. The homology models generated allowed the identification of a putative non-explored, wide, lipophilic pocket at the bottom of the pore of the channel. This pocket was explored by a specifically designed molecular library of 41 retigabine derivatives. Site-specific mutagenesis experiments validated the binding site and the compounds binding pose, involving an extended interaction network with W236, V225, F240, S303, F304, F305 and L312, in the Kv7.2 subtype homotetrameric assembly. Some of the predicted interactions are in accordance with literature data[2] and have been confirmed by the recently released cryo-EM structure of the Kv7.2 subtype.[3] In addition, our results further expand the structure-activity relationship clues for the rational design of Kv7 channels agonists, highlighting the importance of the newly identified lipophilic pocket in drugs-target interaction. The synthesized compounds, were characterized by a Tl^+-based fluorescent HTS assay; the most potent compounds were also studied with patch-clamp electrophysiology. When compared to retigabine, the newly-synthetized compounds showed a more marked leftward shift of the current activation curve, and an enhanced maximal currents. The most potent compounds were also subjected to an extensive in vitro and in vivo preclinical characterization leading to the identification of CP86 as a metabolically stable derivative, with a remarkable CNS distribution. CP86 shows a 4-fold increase in brain concentration and a 80-fold increase in brain-to-blood ratio when compared to retigabine. Moreover, as assessed by photostability experiments, the compound does not generate the toxic photo-induced metabolites, that are responsible for retigabine precipitation in light-exposed tissues, including the retina. Finally, when tested in vivo in the pentylenetetrazol (PTZ) model of acute seizures, CP86 (0.1-1 mg/kg) significantly reduced the latency and severity of PTZ-induced seizures; these effects occurred at one-twelfth of the retigabine (1-3 mg/kg) dose. Most importantly, CP86 treatment significantly reduced PTZ-induced mortality in mice, whereas retigabine was ineffective.[4] Altogether, these data suggest that CP86 is a potent, metabolically-stable, brain permeant, non-phototoxic retigabine derivative with high efficacy against chemically-induced seizures.

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N-Acylethanolamine acid amidase (NAAA): mechanism of palmitoylethanolamide hydrolysis revealed by mechanistic simulations

Laura Scalvini,[a] Andrea Ghidini,[a] Donatella Callegari,[a] Alessio Lodola,[a] Silvia Rivara,[a]

Marco Mor[a] and Daniele Piomelli[b,c,d]

[a] Dipartimento di Scienze degli Alimenti e del Farmaco, Università degli Studi di Parma; [b] Department of Anatomy and Neurobiology, University of California, Irvine, California 92697–4625; [c] Department of Pharmaceutical Sciences, University of California, Irvine, California 92697–4625; [d] Department of Biological Chemistry and Molecular Biology, University of California, Irvine, California 92697–4625

The *N*-terminal cysteine hydrolase *N*-Acylethanolamine acid amidase (NAAA)[1,2] is the enzyme involved in the hydrolytic deactivation of the endogenous lipid messenger, palmitoylethanolamide (PEA), with optimal activity at acidic pH.[3] In this report, we present the results of a multiscale approach, based on classic molecular dynamics (MD) and quantum mechanical/molecular mechanics (QM/MM) simulations coupled with enhanced sampling, applied to the investigation of the mechanism of NAAA-catalyzed PEA hydrolysis.[4]

The proton configuration of catalytic Cys126 and of the surrounding carboxylates was critical to preserve the architecture of NAAA active site. Starting from a stable Michaelis complex of the enzyme and substrate, we reconstructed free-energy surfaces of NAAA acylation and deacylation during PEA hydrolysis. The acylation reaction emerged as the critical step, in which Cys126 acts both as an acid, to protonate the ethanolamine leaving group, and as a nucleophile, to attack the PEA carbonyl carbon. The ethanol fragment of PEA did not appear to contribute to acylation. This result further was further supported by kinetic experiments showing that NAAA hydrolyzes palmitoyl methyl amide (PMA) with high catalytic efficiency. Our multiscale approach has thus led to the identification of a distinctive protonation state and catalytic mechanism for NAAA which accounts for its pH-dependent activity and available mutagenesis data.

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Multiple causes, multiple targets: FAAH as a centerpiece for therapy of multifactorial pathologies.

Leonardo Brunetti, Rosalba Leuci, Antonio Carrieri, Antonio Laghezza, Marco Catto, Luca Piemontese, Paolo Tortorella, Fulvio Loiodice

Dipartimento di Farmacia – Scienze del Farmaco, Università degli Studi di Bari "Aldo Moro".

In the last couple decades, the treatment of chronic and degenerative pathologies has been increasingly studied and has gained significant importance as a topic of pharmaceutical research. Pathologies of this kind include, but are not limited to, neurodegenerative disorders such as Alzheimer's and Parkinson's disease, metabolic disorders such as obesity and diabetes[1], and even cancer. What all these pathologies have in common is a multifactorial nature, which makes them especially hard to treat with standard, single-target therapeutic agents. In this context, Fatty Acid Amide Hydrolase, an enzyme that degrades the main endocannabinoid compound Anandamide (AEA), has become a prominent target, being at the crossroads of many different signaling pathways involving inflammation and sugar and lipid metabolism [2–4].

With this in mind, we set out to screen known agonists of the Peroxisome Proliferator-Activated Receptors (PPARs) for activity towards FAAH, via an enzyme inhibition assay. This approach led to the identification of aryloxyacetic acids as weak, but highly modifiable FAAH inhibitors, with activities in the high micromolar range. Subsequent docking studies suggested that these compounds could bind in a non-covalent fashion to the membrane-access channel of FAAH, with the carboxy group acting as an ionic binding lock and with the aromatic moiety forming hydrophobic interactions with nonpolar side chains in the membrane access channel [5].

Dockings were further expanded in order to assess the viability of the aryloxyacetic scaffold for the development of hybrid compounds with more favorable activity profiles for the therapy of chronic and degenerative diseases. Then, we designed and synthesized a series of hybrid compounds containing an aryloxyacetic moiety connected by methyleneamide linkers to a benzylpiperazine or a benzylpiperidine moiety: these pharmacophoric groups are frequently found in known FAAH and acetylcholinesterase (AChE) inhibitors (such as JZL-195 and donepezil, respectively).

All these compounds proved to be excellent cholinesterase inhibitors, with the IC_{50} values towards AChE ranging from sub-nanomolar to micromolar and a generally lower activity towards butyrylcholinesterase (BChE). Moreover, all but one of the compounds are active as inhibitors of FAAH, with IC_{50} values in the high micromolar range, with longer, more flexible substituents on the phenoxyacetic moiety affording the most significant increase in activity, in accordance with the results of the first screening.

Further research will be directed towards the improvement of the multitarget *in vitro* profile of these compounds and, possibly, towards a better understanding of their effectiveness *in vivo*.

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Influence of the *N*-substituent of (−)-*cis*-*N*-Normetazocine in the modulation of the functional profile at MOR, DOR and KOR: from agonist to antagonist through multitarget ligands

Turnaturi, R.;[a] Parenti C.;[b] Cobos, E.J.;[c] Georgoussi, Z.;[d] Girolamo Calò,[e] Amata Emanuele [a], Maria Dichiara [a], Barbaraci C., Marrazzo A.[a] and Pasquinucci, L. [a]

[a] Department of Drug Sciences and Health – Medicinal Chemistry Section - University of Catania, Viale A. Doria, 6, 95125 Catania, Italy; [b]Department of Drug Sciences and Health – Pharmacology and Toxicology Section - University of Catania Viale A. Doria, 6, 95125 Catania, Italy; [c] Department of Pharmacology, Faculty of Medicine and Institute of Neuroscience, University of Granada, Parque Tecnológico de Ciencias de la Salud, 18100 Armilla, Granada, Spain; [d]Laboratory of Cellular Signaling and Molecular Pharmacology, NCSR "Demokritos", Ag. Paraskevi 15310, Athens, Greece. ; [e]Department of Medical Sciences, Pharmacology section, University of Ferrara, via Fossato di Mortara 19, 44121 Ferrara, Italy

(-)-*cis*-*N*-Normetazocine is a rigid scaffold mimicking the tyramine of endogenous opioid peptides whose different *N*-substituents influence affinity and efficacy versus mu, delta and kappa opioid receptors (MOR, DOR and KOR)[1]. The lead compound LP1, bearing a *N*-phenylpropanamido substituent at the basic nitrogen of (−)-*cis*-*N*-Normetazocine, has been identified as dual-target MOR-agonist/DOR-antagonist ligand[2-4]. LP1 derivatives with different *N*-substituents were synthesized and pharmacologically characterized. In particular, the influence of a second positive charge[5] and the shortening of the *N*-substituent spacer was evaluated. Moreover, the effect of electron-attracting and -donatory groups in the para position of the phenyl ring of LP1 and its replacement with rings with larger steric hindrance[6-7] was explored. Further SARs were obtained through the synthesis of LP1-derivatives with variously alkylated phenyl and their respective tertiary amides obtained through the introduction of a benzyl substituent[8]. Recently, a dual MOR/DOR agonist, endowed of a significant long-lasting antinociceptive effect, was developed through the introduction of the short and flexible 2R/S-methoxy-2-phenylethyl spacer as *N*-substituent[9]. Moreover, its 2*S* diastereoisomer was found to be a potent G-protein biased MOR/DOR agonist[10]. In our SAR studies, the critical role of the basic nitrogen substituent has been confirmed, suggesting the (−)-*cis*-*N*-Normetazocine as a template to reach a specific functional opioid profile, from agonist to antagonist through multitarget ligands.

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Inhibition of non-Hodgkin lymphoma cell growth by pyrrolo[1,2]oxazole derivatives

Marilia Barreca,[a,b] Virginia Spanò,[a] Roberta Rocca,[c,d] Maria Valeria Raimondi,[a] Alessandra Montalbano,[a] Rouli Bai,[e] Chiara Tarantelli,[b] Eugenio Gaudio,[b] Andrea Prota,[f] Michel Steinmetz,[f] Stefano Alcaro,[c,g] Ernest Hamel,[e] Francesco Bertoni,[b,h] and Paola Barraja. [a]

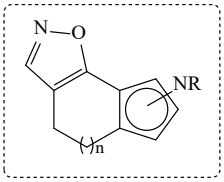
[a] *Department of Biological, Chemical and Pharmaceutical Sciences and Technologies (STEBICEF), University of Palermo, Italy;* [b] *Institute of Oncology Research, USI, Bellinzona, Switzerland;* [c] *Net4Science srl, Academic Spinoff, Magna Græcia University, Viale Europa, 88100, Catanzaro, Italy;* [d] *Department of Experimental and Clinical Medicine, Magna Græcia University, Viale Europa, 88100, Catanzaro, Italy;* [e] *Molecular Pharmacology Branch, Developmental Therapeutics Program, Frederick National Laboratory for Cancer Research, National Cancer Institute, Maryland, United States;* [f] *Laboratory of Biomolecular Research, Department of Biology and Chemistry, Paul Scherrer Institut, 5232 Villigen, Switzerland;* [g] *Department of Health Sciences, University Magna Græcia of Catanzaro, Italy;* [h] *Oncology Institute of Southern Switzerland, Bellinzona, Switzerland.*

Lymphomas are among the top ten most common cancers and represent a heterogeneous group of disorders. Despite large improvements during the years, still too many individuals succumb due to their disease, indicating the need for novel therapeutic agents. An example is given by the diffuse large B-cell lymphoma (DLBCL), the commonest lymphoma, in which up to 30-40% of all cases are not cured by the standard chemo-immunotherapy regimen R-CHOP. Anti-tubulin agents are very active in lymphomas [1] and are included in fundamental chemotherapy schemes (R-CHOP, ABVD, BEACOP) as well as in the innovative therapeutic approaches utilizing antibody-drug conjugates (ADCs) such as brentuximab vedotin and polatuzumab vedotin.

The [1,2]oxazole ring is a valuable chemical feature for the design of tubulin-binding agents. Recently, we have devoted our efforts to the investigation of a large family of pyrrolo[1,2]oxazole derivatives, with wide variability of chemical scaffolds and substituents [2,3]. We now present our recent results against four lymphoma histotypes: germinal center B-cell and activated DLBCL (GCB-DLBCL and ABC-DLBCL), marginal zone lymphoma (MZL) and mantle cell lymphoma (MCL). Several derivatives showed anti-proliferative activity in at least one lymphoma model, with IC_{50} values between the low micromolar and nanomolar range.

Insight on the mechanism of action indicated G2/M phase arrest and induction of apoptosis through strong inhibition of tubulin polymerization and colchicine binding to tubulin (Frederick National Laboratory for Cancer Research). Molecular modelling studies revealed strong interactions with tubulin and a peculiar binding mode, characterized by the methoxybenzyl portion placed similarly to colchicine (Magna Graecia University). Furthermore, crystallographic data confirmed the clear perturbation of the colchicine site with the βT7 and αT5 loops of tubulin rotated to accommodate the ligands (PSI Institut).

In conclusion, our recent results indicate that pyrrolo[1,2]oxazole derivatives are promising agents for the treatment of lymphoma.



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A new strategy to overcome multidrug resistance (MDR) in cancer cells: P-gp and hCAXII multitarget inhibitors

Braconi, L.;[a] Coronnello, M.;[b] Nocentini, A.;[a] Bartolucci, G.;[a] Riganti, C.;[c] Romanelli, M.N.;[a] Supuran, C.T.;[a] Dei, S.[a] and Teodori, E.[a]

[a] Department of NEUROFARBA, University of Florence, Via Ugo Schiff 6, 50019 Sesto Fiorentino (FI), Italy; [b] Department of Health Sciences, University of Florence, Viale Pieraccini 6, 50139 Firenze, Italy; [c] Department of Oncology, University of Torino, Via Santena 5/bis, 10126 Torino, Italy.

MDR is a type of acquired resistance and is the main cause of chemotherapy treatment failure. It is often related to the overexpression of ABC transmembrane proteins which work as efflux pumps, reducing the intracellular concentration of the anticancer drugs below their active dose. Searching for new strategies to overcome P-gp-mediated MDR, the evidence of a physical association between P-gp and hCAXII allowed us to discover new MDR reversing agents with dual inhibitory effects. P-gp is the first ABC transporter to be discovered playing a role in MDR[1]. hCAXII is a transmembrane-bound CA isoform and is overexpressed with P-gp in several resistant cancer cells, such as HT29/DX and A549/DX cells. Herein, the pharmacological inhibition of hCAXII alters the optimal pH for P-gp ATPase activity, reducing its efflux effect[2]. Thus, new series of dual P-gp/hCAXII inhibitors, containing scaffolds found in potent P-gp ligands, and a coumarin moiety to target hCAXII, were designed and synthesized (Figure 1).

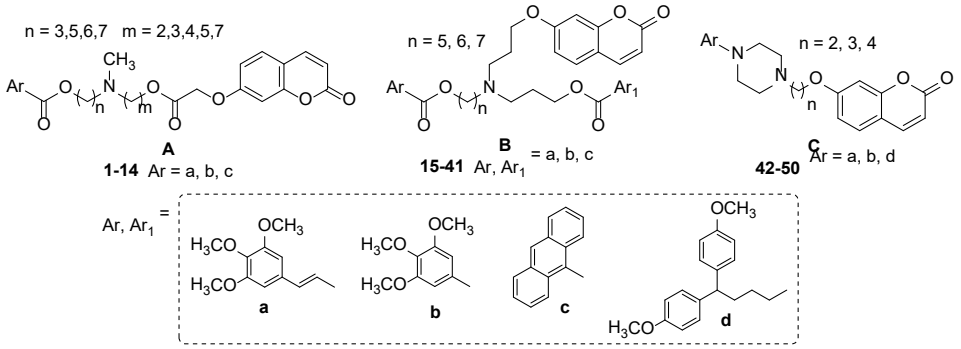

Figure 1. *Dual P-gp/hCAXII inhibitors.*

Compounds **1**-**14** (**A**) increased the antineoplastic effect of Doxorubicin on resistant K562/DX cells, which overexpressed only P-gp, and inhibited the hCAXII isoform in the nanomolar range[3]. Based on these promising results, we introduced a propyloxycoumarin moiety on the nitrogen atom of the *N*,*N*-bis(alkanol)amine diester scaffold (**B**), which displayed high P-gp inhibitory effects[4]. Interestingly, derivatives **15**-**41** (**B**) displayed higher MDR reversal effects on HT29/DX and A549/DX cell lines, which overexpressed both proteins, than on K562/DX cells. Moreover, to further investigate new dual P-gp/hCAXII inhibitors, we designed and synthesized a series of *N*-alkyloxycoumarin-*N*-(methoxysubstituted)aryl piperazines (**C**). The piperazine ring and aryl moieties were chosen based on their presence in very potent MDR reversers[5]. Preliminary results showed that compounds **42**-**50** (**C**) maintained a good inhibitory effect on both P-gp and hCAXII.
Therefore, finding new strategies to overcome MDR still remains a great challenge, but we have found valuable candidates for selective inhibition of P-gp and hCAXII on MDR cancer cells.

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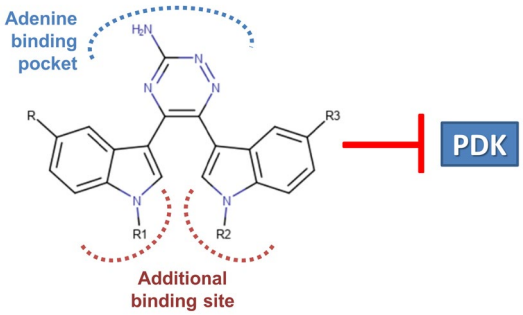
Synthesis and preclinical evaluation of a new generation of 1,2,4-triazine-based PDK modulators: a novel therapeutic approach to halt cancer growth

Carbone, D.;[a] Pecoraro, C.;[a] De Franco M.;[b] Parrino, B.;[a] Cascioferro, S.;[a] Cirrincione, G.;[a] Gandin, V.;[b] and Diana, P.[a]

[a]*Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche (STEBICEF), Università degli Studi di Palermo, Via Archirafi 32, 90123 Palermo, Italy*
[b]*Dipartimento di Scienze del Farmaco, Università degli Studi di Padova, Via F. Marzolo 5, 35131 Padova, Italy.*

Pyruvate dehydrogenase kinases (PDKs, isoforms 1-4) are serine/threonine kinases, whose primary known function involves the glucose metabolism by inactivating the pyruvate dehydrogenase complex (PDC). PDC acts as a gatekeeper enzyme for cellular energy metabolism by catalyzing irreversible decarboxylation of pyruvate into acetyl-CoA. Inhibition of PDC activity by PDK has been associated with poor prognosis in cancer as PDKs are commonly overexpressed in several cancer types. Such increased expression of PDKs in cancer cells induces a perturbation of the PDH/PDK axis, known as Warburg effect, with an increase in aerobic glycolysis and a reduction in mitochondrial oxidation, thus enabling cancer cell proliferation, migration/invasion ability, resistance to apoptosis and stemness. [1] Consequently, inhibition of PDK is emerging as a novel attractive therapeutic strategy for the development of selective anticancer agents targeting cancer cells and cancer stem cells. Relatively few PDK inhibitors have been up to now disclosed, some of which interacts with the amino acid residues of ATP binding site of PDK, through the formation of hydrogen bonds, causing local conformational changes with complete disordering of the ATP lid. [2]
In an effort to find new PDK inhibitors, we rationally designed and synthesized a new class of 5,6-bis-(indolyl)-[1,2,4]triazin-3-yl-amines, which due to the presence of two nitrogen atoms, hydrogen bond acceptors, and an amino group, hydrogen bond donor, could efficiently bind to the adenine region of PDK ATP-binding site. In addition, the presence of the two extra nitrogen atoms in the indole moieties could increase the possible fits in the ATP-binding cavity which requires well positioned H bond donor/acceptor systems.



Preliminary biochemical screenings showed that all synthesized compounds are potent and subtype-selective inhibitors of PDK, with major selectivity for PDK1 and PDK4 isoforms. Interestingly, 2D and 3D cell studies revealed their ability to induce human cancer cell death in the low micromolar range, being extremely effective against KRAS mutated cancer cells. Detailed cellular mechanistic studies performed with the most promising derivatives confirmed their ability to hamper the PDC/PDK axis, thus determining mitochondrial damage, and ultimately leading to cancer cell death by reversing the Warburg effect. Further cellular and *in vivo* validation studies are in progress.

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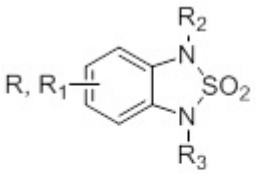
Unraveling the interaction mechanism of a benzothiadiazole-2,2-dioxide derivative with STAT3: towards novel direct inhibitors

Matteo Mori [a], Ettore Gilardoni [a], Luca Regazzoni [a], Alessandro Pedretti [a], Diego Colombo [b], Gary Parkinson [c], Akira Asai [d], Giulia Cazzaniga [a], Fiorella Meneghetti [a], Stefania Villa [a] and Arianna Gelain [a]

[a] *Department of Pharmaceutical Sciences, University of Milan, via L. Mangiagalli 25, 20133 Milan, Italy*
[b] *Department of Medical Biotechnology and Translational Medicine, University of Milan, via C. Saldini 50, 20133 Milan, Italy*
[c] *Department of Pharmaceutical and Biological Chemistry – UCL School of Pharmacy, University College London, 29/39 Brunswick Square, WC1N 1AX London, United Kingdom*
[d] *Center for Drug Discovery – Graduate School of Pharmaceutical Sciences, University of Shizuoka, 52-1 Yada, Suruga-ku, 422-8526 Shizuoka, Japan*

Signal Transducer and Activator of Transcription 3 (STAT3) participates in oncogenesis by stimulating cell proliferation and preventing apoptosis; this protein has been validated as a suitable and selective target for anticancer therapy [1,2]. Starting from a virtual screening approach on STAT3-SH2 domain, we identified 5,6-dimethyl-1*H*,3*H*-2,1,3-benzothiadiazole-2,2-dioxide (**1**) as a potential inhibitor. Therefore, we synthesized and tested a series of derivatives (Figure 1), among which benzosulfamide **1** showed a significant activity (IC_{50} = 15.8 ± 0.6 µM by AlphaScreen-based assay) as a direct STAT3 inhibitor. Hence, an in-depth investigation through mass spectrometry, liquid chromatography and UV spectroscopy studies was carried out, shedding light on its intriguing mechanism of interaction, also involving cysteine residues located around the SH2 domain [3].



R = H, Cl, CH_3, NO_2, etc.
R_1 = H, Br, CH_3
R_2, R_3 = H, CH_3, CH_2Ph

Figure 1. Benzothiadiazole derivatives of compound **1**.

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Flow-based redox biotransformations for food and pharma applications

Francesca Annunziata,[a] Martina L. Contente,[b] Raffaella Gandolfi,[a] Paola Conti,[a] Andrea Pinto,[b] Lucia Tamborini[a]

[a] Department of Pharmaceutical Sciences, University of Milan, Via Mangiagalli 25, 20133 Milan, Italy; [b] Department of Food, Environmental and Nutritional Sciences, University of Milan, Via Celoria 2, 20133 Milan, Italy.

Biocatalysis and flow chemistry are ideal partners for accessing novel chemical spaces and define efficient and sustainable synthetic tools with high level of intensification [1]. In this context, in the last few years, we exploited continuous flow biocatalysis to develop greener and scalable routes for the synthesis of high value chemicals and active pharmaceutical ingredients (APIs).
In particular, we focused our attention on biocatalytic redox reactions, which are very attractive because they often occur with regio- and stereo-selectivity under mild and environmentally friendly conditions. Here, two different applications, using both whole cells and isolated enzymes, are presented.

i) Enantioselective reduction of β-ketonitriles
Immobilized whole cells of *Rhodotorula rubra* MIM 147 have been exploited in a fully automated system for the enantioselective synthesis of β-hydroxynitriles starting from β-ketonitriles, exploiting a choline chloride/glucose natural deep eutectic solvent (NADES) having a dual function, as a co-solvent and as a source of glucose, fundamental for the cofactor regeneration. The continuous system allowed for an automated work-up and purification procedure, through an in-line extraction with ethyl acetate followed by liquid-liquid separation and removal of the unreacted substrate using polymer supported benzylamine. The optimized protocol allowed the isolation of a key building block for the synthesis of the antidepressant drug duloxetine, *i.e.*, (*S*)-3-hydroxy-3-(thiophen-2-yl)propanenitrile, in 60 minutes of residence time with >90% conversion and >99% e.e. and resulted to be versatile for the enantioselective reduction of different β-ketonitriles.

ii) Oxidation of tyrosol to hydroxytyrosol
Tyrosol (Ty) and hydroxytyrosol (HTy) are valuable dietary phenolic compounds present in olive oil and wine and are shown to possess a range of biological effects, including antioxidant, and antimicrobial effects [2]. The availability of gram amounts of pure Ty, HTy, their metabolites and derivatives is highly appealing for a deep biological evaluation. In this context, an efficient biocatalyzed protocol for the transformation of Ty into high-value HTy and for the obtainment of their acetylated metabolites was developed. The first step was the oxidation of Ty by a free tyrosinase from *Agaricus bisporus* in presence of oxygen and ascorbic acid. The aqueous flow stream was then extracted in-line with ethyl acetate and the aqueous layer, containing the biocatalyst and the excess of ascorbic acid, was recirculated to improve the economy of the protocol in a self-sufficient closed-loop system. The organic phase was purified in-line, thanks to a catch and release procedure, using supported boronic acid to trap HTy, leaving unreacted Ty in solution. To obtain the acetyl metabolites, a bioreactor packed with an immobilized acyltransferase from *Mycobacterium smegmatis* (MsAcT) was used [3]. With this modular set up, HTy was obtained with an isolated yield of 75%, whereas the acetyl metabolites showed yields up to 80% in 10 minutes.

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Stability of chlorogenic acid as model system after household microwave treatment

Federica Ianni [a], *Carolina Barola* [b], *Francesca Blasi* [a], *Simone Moretti* [b], *Roberta Galarini* [b], *Lina Cossignani* [a]

[a] *Food Science and Nutrition Section, Department of Pharmaceutical Sciences, University of Perugia, 06126 Perugia, Italy*
[b] *Istituto Zooprofilattico Sperimentale dell'Umbria e delle Marche "Togo Rosati", 06126 Perugia, Italy*

Several health benefits have been associated with the consumption of foods and drinks rich in chlorogenic acid [1]. However, besides the properties of this phenolic secondary metabolite, named also as 5-caffeoylquinic acid (5-CQA), an important issue is represented by its low stability during food processing or extraction procedures which result into isomerization to neochlorogenic acid (3-CQA) and cryptochlorogenic acid (4-CQA) as well as in the formation of further products [2]. Figure 1 shows the structure of the three main CQA isomers.

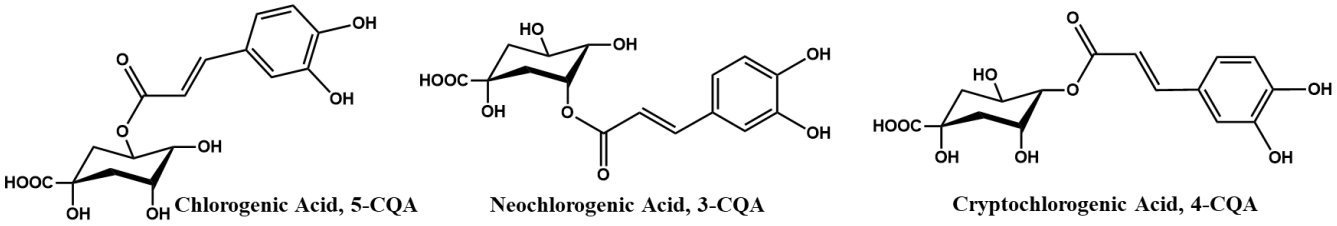

Figure 1. Structure of the investigated molecules.

According to a recent study [3], a notable reduction of 5-CQA content in *Lycium barbarum* leaf extracts after household preparation by microwave was observed, in respect to the more traditional decoction and infusion procedures. Based on this evidence, the 5-CQA reactivity in water was evaluated by simulating the domestic microwave procedure in the more drastic conditions, using as model system aqueous solutions of standard 5-CQA. Specifically, the results obtained by the use of commercial waters, characterized by a different fixed residue, were compared with those obtained by the use of analytical grade waters.

An optimized HPLC-UV method allowed to monitor the 5-CQA conversion to its main isomers, while the identification and structural elucidation of further transformation products was performed by LC-HRMS/MS. The results highlighted a different 5-CQA isomerization degree depending on the specific water sample, and the formation of oxidation derivatives of CQA isomers. The study highlights the importance of the analytical control to monitor 5-CQA transformation during microwave treatment. This represents a first stage which could allow minimizing CQA decomposition while preserving the potential health promoting effects of such bioactive constituent in foods and beverages.

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Comparison of different extraction methods to recover bioactive compounds from corn waste (*Zea mays L.*)

I. Frosi[a], I. Montagna[a], C. Milanese[b], A. Papetti[a]

[a] Drug Sciences Department,Viale Taramelli 12/14, Pavia, Italy; [b] C.S.G.I and Chemistry Department, Viale Taramelli 16, Pavia, Italy

The minimization and reutilization of food waste is extremely relevant nowadays [1]. The European Commission itself has defined long-term strategies for a sustainable development, in order to support a circular economy and give a second life to wastes [2]. Following these guidelines, we focus our attention on the valorization of corn wastes (*Zea mays L.*), a promising source of chemically different bioactives with healthy properties [3,4].
The aim of our project is to recover phenolic compounds suitable for food supplements from Lombard corn cob. In particular, the efficiency of a conventional extraction method was compared to an innovative extraction technique assisted by microwaves. These two green extraction methods were set-up to recover phenolic compounds using different solvents, traditional hydro-alcoholic mixtures and innovative natural eutectic mixtures with the so-called deep eutectic solvents strategy [5,6].
To maximize the recovery of bioactives, the influence of various parameters on extraction yield was studied using experimental designs and the composition of each extract was monitored by different analytical techniques. High-performance liquid chromatography investigation on the chemical composition of corn cob revealed the presence of different polyphenolic compounds independently from the extraction methods and solvents tested, pointing out the possible beneficial properties and suggesting further screenings. Results indicated that the higher extraction yields were generally obtained by means of innovative microwave assisted extraction with traditional hydro-alcoholic mixtures. Extraction time is significantly reduced using microwaves, bringing to the reduction of energy consumption compared to conventional heating method. The efficiency of the innovative technique is probably related to the plant matrix's cell rupture induced by microwave irradiation, encouraging the release of bioactives. Further scanning electron microscopy (SEM) analysis will be performed to analyse the microstructure of corn cob before and after microwave irradiation to confirm this mechanism.

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Valorization of food wastes and residues through glycosidases

Martina L. Contente [a], Giorgia Catinella [a], Sabrina Dallavalle [a], Gigliola Borgonovo [a], Andrea Pinto [a]

[a] Department of Food, Environmental and Nutritional Sciences, University of Milan, Via Celoria 2, 20133 Milan, Italy.

Food processing waste and residues hold significant potential for biotransformation into a plethora of value-added compounds with novel applications in the food, pharmaceutical and cosmetic industries. Enzymes as biocatalysts offer unique advantages over traditional synthetic processes with regard to eco-sustainability and processes efficiency. Notably, enzymes have been applied to food products since early times of civilization, for instance in the preparation of bread, wine or milk. Recently, glycosidases are becoming key tools within the food industry because of their ability to hydrolyze glycosidic bonds in a selective, clean and efficient way.

Here three different examples of biotrasformations of agri-food wastes/residues into high-value products are reported:

i) **Efficient transformation of picrocrocin into safranal**. Among the glycosides one of the main components of saffron residues is picrocrocin, responsible for the bitter taste in saffron spice [1]. After partial purification of the extract, the natural precious safranal has been obtained in a two step-reaction: the first one involves the extremophilic glycosidase from *Alicyclobacillus acidiphilus* which in 15 min generates 4-hydroxy-safranal with complete conversion. The second one based on a simple acid catalysis forms safranal. Starting from natural material and using biocatalysts, this aroma can be commercialized as natural too, thus increasing its market value. Moreover, taking into account safranal beneficial properties, high concentrations of this bioactive compound in the spice or in the spice extract may contribute in making saffron a potential functional food [2].

ii) **Multi-enzymatic cascade biotransformations**. Oleuropein, one of the main constituents of olive leaves and fruits [3] has been biotransformed using a halotolerant glycosidase from *Alicyclobacillus herbarius* to generate the corresponding aglycone well known for its anticancer, anti-Alzheimer and anti-inflammatory activities [4]. This intermediate has been directly employed as a substrate of a transferase from *Mycobacterium smegmatis* for the preparation of hydroxytyrosol, one the most potent antioxidant in nature.

iii) **Multi-step one-pot enzymatic reaction.** From grapefruit waste, glycosides typically found in citrus species such as hesperidin, neoesperidin and naringin [5] have been isolated as single compounds and together as an extract. Due to the biocatalyst selectivity only hesperidin has been biotransformed through a one-pot, 2-step reaction involving an α-rhamnosidase and a glycosidase from *Halothermothrix orenii,* a halophilic and thermophilic bacterium. The final hesperetin aglycon is a value-added natural product for its bioactive properties as antioxidant and neuroprotective [6].

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A sulfonyl fluoride derivative selectively inhibits EGFR$^{L858R/T790M/C797S}$ by covalent modification of the catalytic lysine

Francesca Ferlenghi[a], *Federica Vacondio*[a], *Riccardo Castelli*[a], *Nicole Bozza*[a], *Giuseppe Marseglia*[a], *Laura Scalvini*[a], *Silvia Rivara*[a], *Alessio Lodola*[b], *Silvia La Monica*[b], *Roberta Minari*[c], *Piergiorgio Petronini*[b], *Roberta Alfieri*[b], *Marcello Tiseo*[b,c] *and Marco Mor*[a]

[a]*Department of Food and Drug, University of Parma;* [b]*Department of Medicine and Surgery, University of Parma;* [c]*Medical Oncology, University Hospital of Parma.*

Insurgence of the C797S mutation in EGFR kinase is one of the most frequent mechanisms of resistance to osimertinib in the treatment of non-small cell lung cancer (NSCLC) [1]. To overcome acquired resistances, the seek for EGFR inhibitors able to bind lysine 745 (K745), a residue fundamental for the kinase activity, appears as a promising strategy [2]. Within a panel of electrophilic compounds designed and synthesized in our lab, UPR1444 (**Figure 1A**) emerged as the most promising candidate. It possesses a benzenesulfonyl fluoride warhead that is expected to react with K745 of EGFR, similarly to what had been observed for the non-selective kinase probe XO44 [2], and the 2,4-dianilino-pyrimidine scaffold found in third-generation EGFR inhibitors, which should confer selectivity for EGFR. This contribution illustrates the design, synthesis and inhibition mechanism of UPR1444 on recombinant EGFR$^{L858R/T790M/C797S}$. In enzymatic assays, UPR1444 half-maximal inhibitory concentration (IC_{50}) on EGFR$^{L858R/T790M/C797S}$ activity proved 150-fold lower than osimertinib IC_{50} after 3 h of preincubation (**Figure 1B**). On the other hand, UPR1444 showed a potency comparable to that of osimertinib on wild-type EGFR while, as the reference sulfonyl fluoride XO44, it failed to inhibit the EGFR$^{del19/T790M/C797S}$ activated form. A rapid dilution assay showed that EGFR$^{L858R/T790M/C797S}$ inhibition is stable after 30 min from dilution; conversely, in the same conditions, UPR1444 allowed over 50% recovery of EGFR wild type activity. Moreover, UPR1444 proved a remarkable selectivity when tested on a panel of kinases inhibited by XO44. To validate the covalent modification of K745, EGFR$^{L858R/T790M/C797S}$ was incubated for 3 h with UPR1444 and then subjected to tryptic digestion before high-resolution mass spectrometry analysis. The peptide IPVAIK^{745}ELR was found with a mass shift compatible with the sulfonylation of K745 by UPR1444, which was confirmed *via* tandem mass spectrometry analysis. We finally assayed UPR1444 on a Ba/F_3 cell line expressing EGFR$^{L858R/T790M/C797S}$ [3], where UPR1444 proved over six times more potent than osimertinib at inhibiting both EGFR autophosphorylation and proliferation (**Figure 2**). The data here presented pointed out UPR1444 as the first example of a selective lysine-sulfonylating agent able to inhibit EGFR$^{L858R/T790M/C797S}$ by an irreversible mechanism.

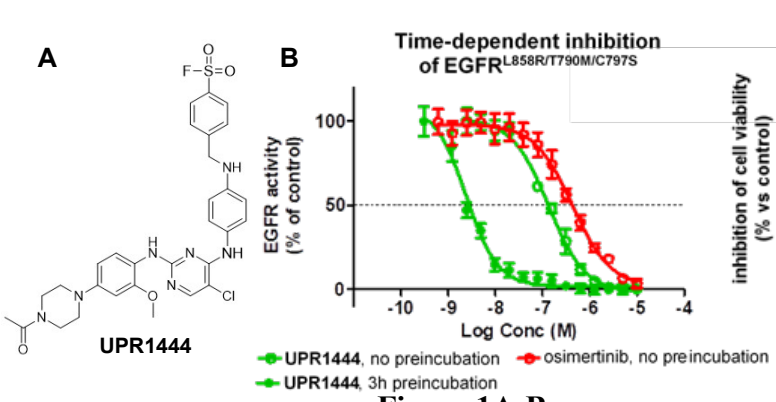

Figure 1A-B

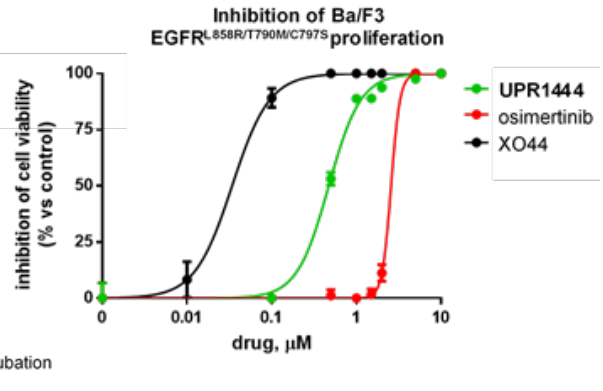

Figure 2

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Novel potential DPP IV/ CA II inhibitors for the treatment of Type 2 Diabetes

Artasensi A.[a], Angeli A.[b], Lammi C.[a], Supuran C.[b], Vistoli G.[a], Fumagalli L.[a]

[a] Department of Pharmaceutical Sciences "Pietro Pratesi", University of Milan, Via Mangiagalli 25, I-20133 Milan, Italy; [b] Department of Pharmaceutical Sciences "NEUROFARBA", University of Florence, Via Ugo Schiff 6, 50019 Sesto Fiorentino, Florence, Italy.

Diabetes syndrome is characterized by high blood sugar levels, which trigger a pro-inflammatory response that causes micro-vascular damage and leads to serious chronic complications such as blindness, renal failure and diabetes-accelerated atherosclerosis [1,2]. Furthermore, several major enzymes are abnormally expressed or show anomalous activity in this state of metabolic disturbance, so they might be interesting targets in drug discovery. Hence, the development of multitarget drugs, which could reduce hyperglycemia and slow down the progression of complications, may offer a valuable therapeutic option.

In order to find new therapeutic strategies, repurposing and morphing approaches were applied on WB-4101, a well-known adrenergic ligand. Repurposing [3] could minimize the risk of failure in future late-stage clinical trials due to toxicity, while morphing approach could allow to introduce/modulate the activity towards old and new targets, to retain satisfactory drug likeness properties and to avoid issues in the patent landscape.

Repurposing studies found out that WB-4101 can conveniently fit the binding pockets of two enzymes, namely Dipeptidyl Peptidase IV (DPP IV) and Carbonic Anhydrase II (CA II) involved in Type 2 Diabetes Mellitus (T2D), while failing to stabilize all required interactions. Indeed, WB-4101 lacks a moiety able to interact with a key arginine residue in the DPP IV pocket and with the zinc ion of the CA II.

Our class of compounds were designed with the purpose of satisfying both these needs by inserting a sulfonamide function, which is a well-known chelating group for the Zinc ion and can be seen as a valid bioisostere of the carboxyl group to interact with the arginine [4]. In addition, this moiety was inserted in *para* position on the phenoxy ring based on previous investigations, which demonstrated that this substitution abrogates or strongly reduces the adrenergic affinity.

Computational and pharmacological investigations were performed also on CA V, a mitochondrial carbonic anhydrase isoform involved in glucose metabolism [5].

Here, we report the investigation of several derivatives for expanding the structure activity relationship (SAR) of this new class of compounds and to further improve the rational ligand design.

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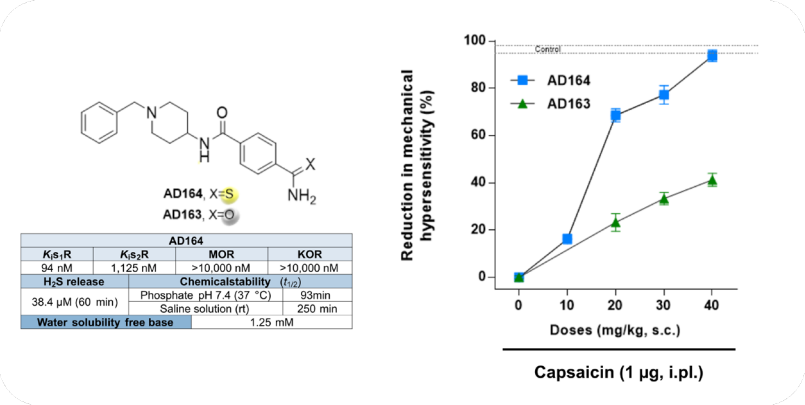
Design, synthesis and pharmacological evaluation of 4-carbamothioylphenyl sigma-1 receptor antagonists for pain treatment

Maria Dichiara,[a] Antonia Artacho-Cordón,[b] Rita Turnaturi,[a] Miriam Santos-Caballero,[b] Elisabetta Tomarchio,[a] Maria Tindara Ignazzitto,[a] Lorella Pasquinucci,[a] Carla Barbaraci,[a] Agostino Marrazzo,[a] Enrique J. Cobos,[b] and Emanuele Amata[a]

[a] Department of Drug and Health Sciences, Medicinal Chemistry Section, Università degli Studi di Catania, 95125 Catania, Italy; [b] Department of Pharmacology and Neurosciences Institute (Biomedical Research Center), University of Granada and Biosanitary Research Institute ibs.Granada, 18016 Granada, Spain

Pain is a global health burden, with millions of people suffering from chronic pain. Current analgesics often show restricted efficacy or side effects which limit their use.
Sigma receptors, denoted as sigma-1 (σ_1) and sigma-2 (σ_2) receptor, are involved in several biological and pathological conditions. A wide number of data support the modulatory role of σ_1 receptor antagonists in nociception. The selective σ_1 receptor antagonist E-52862 (S1RA) is undergoing phase II clinical trial for the treatment of neuropathic pain of different etiologies [1].
Hydrogen sulfide (H_2S) is an endogenous gasotransmitter involved in the modulation of the daily cellular activities as well as cytotoxic events, including nociceptive processes. The H_2S exogenous administration showed a reduction of the nociceptive response in diverse animal models of pain. At this regard, the H_2S-releasing anti-inflammatory drug ATB-346 has successfully completed phase II clinical in osteoarthritis [2].
To this extent, we turned our interest on the development of novel hybrid compounds able to release H_2S and to bind σ_1 receptor as candidates for pain treatment. The purpose is to obtain improved analgesic properties when compared to σ_1 receptor antagonists or H_2S-donor alone.



AD164			
$K_i\sigma_1R$	$K_i\sigma_2R$	MOR	KOR
94 nM	1,125 nM	>10,000 nM	>10,000 nM
H_2S release	Chemicalstability ($t_{1/2}$)		
38.4 µM (60 min)	Phosphate pH 7.4 (37 °C)	93min	
	Saline solution (rt)	250 min	
Water solubility free base	1.25 mM		

We first started to investigate the role of the σ_1 receptor antagonist BD-1063 or H_2S-donor alone and the association of both mechanisms in a capsaicin-induced mechanical hypersensitivity. Later, four hybrid ligands have been designed having a 4-carbamothioylphenyl moiety covalently joined to appropriate amines. To better dig into the precise mechanism, cognate derivatives lacking the thioamide function have been prepared as negative control. All the compounds have been evaluated for affinity at σ and opioid receptors and ability to release H_2S. The major hurdle was to find hybrid ligands with a balanced activity when evaluated in vivo. Indeed, to have a measurable synergic effect, the σ receptor component should not prevail over the H_2S-donor activity, and vice versa. The analgesic properties of the synthetized positive/negative ligands have been evaluated in co-administration with the selective σ_1 receptor agonist PRE-084. Candidate with the desired in vivo pharmacological profile has been further evaluated to assess the in vitro pharmacokinetic behavior.

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Identification of novel Sigma 1 receptor antagonists based on arylalkanolamine scaffold for the treatment of neuropathic pain

Giacomo Rossino[a], Pasquale Linciano[a], Daniela Rossi[a], Marco Peviani[b], Giulio Massimo Dondio[c], Annalisa Canta[d], Guido Cavaletti[d], Simona Collina[a]

[a] Department of Drug Sciences, University of Pavia, Viale Taramelli 12, Pavia, Italy; [b] Department of Biology and Biotechnology "L. Spallanzani", University of Pavia, Via Ferrata 9, Pavia, Italy; [c] Aphad Srl, Via della Resistenza 65, Buccinasco (MI), Italy; [d] Experimental Neurology Unit, University of Milano-Bicocca, Monza, Italy.

Neuropathic pain (NP) is long-term pain caused by damages in pain-signaling pathways. It is a debilitating disorder that affects up to 10% of world population and represents a significant burden for public health systems [1]. Most of NP treatments available to date rely on opioid analgesics, which are effective in alleviating pain but have severe risks (e.g. respiratory depression, nausea, dependence and abuse). Thus, there is a significant and unmet need for non-opioid pain medications. Sigma 1 Receptor (S1R) has emerged as an alternative therapeutic target for the modulation of pain-related neuropathways [2], and S1R antagonist are being investigated for their promising analgesic effects [3]. Herein we report on the synthesis and biological evaluation of a small library of S1R antagonists based on arylalkanolamine scaffold (Figure 1). After determination of affinity toward S1R and selectivity over Sigma 2 Receptor (S2R), the agonist/antagonist profile was drawn by evaluating the effects on i) nerve growth factor induced neurite outgrowth and ii) Aquaporins-mediated water permeability in presence and absence of oxidative stress. MCL-752 emerged as the hit compound worthy of further investigation both *in vitro* and *in vivo*. Calcium influx assay confirmed its S1R antagonist activity and the evaluation of its cytotoxic activity against a wide panel of cancer cell lines demonstrated its safety. Moreover, MCL-752 resulted metabolically stable in diverse biological matrices (i.e. blood, plasma and liver microsomes) of different species (i.e. mouse, rat, dog and human). Finally, the analgesic activity of MCL-752 was evaluated in two animal models of NP: formalin induced licking paw test and Chung's model [4,5]. The results clearly indicate that our hit compound is effective in alleviating pain at safe doses, thus supporting the idea that S1R antagonists could be used as analgesics in place of opioid medications. These findings prompted us to patent our new class of S1R antagonists for the treatment of pain [6].

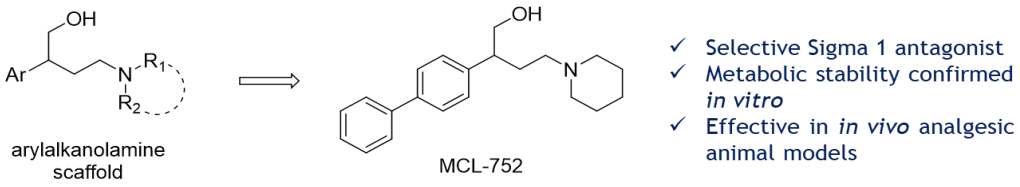

Figure 1. Common scaffold of the developed library and structure of hit compound MCL-752.

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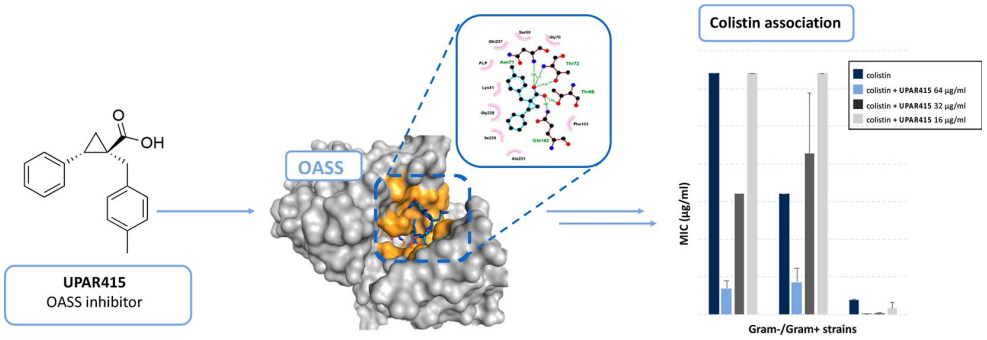
Investigational studies on cyclopropane- carboxylic acid derivatives targeting O-acetylserine sulfhydrylase as colistin adjuvants

Giannamaria Annunziato[a], Costanza Spadini[b], Nina Franko[c], Marco Pieroni[a], Mattia Iannarelli[b], Marialaura Marchetti[d], Stefano Bettati[e], Andrea Mozzarelli[c], Clotilde Silvia Cabassi[b], Barbara Campanini[c], Gabriele Costantino[a]

[a] P4T Group, Department of Food and Drugs, University of Parma, 43124 Parma, Italy; [b] Operative Unit of Animals Infectious Diseases, Department of Veterinary Science, University of Parma, 43126 Parma, Italy; [c]Laboratory of Biochemistry and Molecular Biology, Department of Food and Drugs, University of Parma, 43124 Parma, Italy; [d] Biopharmanet-TEC Interdepartmental Center, University of Parma, 43124 Parma, Italy; [e] Department of Medicine and Surgery University of Parma, 43125 Parma, Italy.

Antibacterial adjuvants are of great significance, since they allow the therapeutic dose of conventional antibiotics to be lowered and reduce the insurgence of antibiotic resistance. We reported that an O-acetylserine sulfhydrylase (OASS) inhibitor can be used as a colistin adjuvant to treat infections caused by Gram-positive and Gram-negative pathogens. A compound, UPAR415, that binds OASS with a nM dissociation constant was tested as an adjuvant of colistin against six critical pathogens responsible for infections spreading worldwide, *Escherichia coli*, Salmonella enterica serovar Typhimurium, *Klebisiella pneumoniae*, *Staphylococcus aureus*, *methicillin-resistant Staphylococcus aureus*, and *Staphylococcus pseudintermedius*. UPAR415 showed promising synergistic or additive activities against all of them. Knockout experiments confirmed the intracellular target engagement supporting the proposed mechanism of action. Moreover, compound toxicity was evaluated by means of its hemolytic activity against sheep defibrinated blood cells, showing a good safety profile [1]. On these bases, we decided to develop a new class of adjuvants to provide further structure–activity relationship studies. A series of UPAR415 derivatives has been design and synthesized, and most of them still maintain good activities toward both OASS isoforms. The most promising compounds, endowed with good activity *in-vitro* and good toxicity profile, were tested in association with colistin and we are pleased to notice that the new derivatives showed synergistic activity at a concentration 8 folds lower than UPAR415.

Our results suggest the possibility to identify compounds able to selectively target the microbial reductive sulfur assimilation pathway by interfering with both OASS isoforms [2], providing a good starting point supporting OASS as potential pharmaceutical target to develop a new class of antimicrobial adjuvant.



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Phenotype screening of a bisindole chemical library identifies URB1483 as a new antileishmanial agent with topoisomerase IB as possible molecular target

Simone Lucarini[a], *Aurora Diotallevi*[a], *Gloria Buffi*[a], *Laura Scalvini*[b], *Alessio Lodola*[b], *Gianfranco Favi*[a], *Silvia Castelli*[c], *Alessandro Desideri*[c] *and Luca Galluzzi*[a]

[a] *Department of Biomolecular Sciences, University of Urbino Carlo Bo;* [b] *Department of Food and Drug, University of Parma;* [c] *Department of Biology, University of Rome Tor Vergata.*

Leishmaniasis is one of the most dangerous neglected tropical diseases, second only to malaria in parasitic causes of death. [1] Caused by global warming, the endemic regions of leishmaniasis are continuously spreading to non-tropical areas, including Europe. So far, no vaccine against leishmaniasis is on the market. [2] Approved drugs are currently limited and/or exorbitantly priced (i.e. amphothericin B; paromomycin; miltefosine; pentamidine) with few of them effective on antimonial-resistant *Leishmania* strains. Moreover, the use of these agents on infected patients is seriously hampered by the insurgence of acute and/or chronic toxicity. Therefore, there is an urgent need for developing safe, effective, and affordable drugs for the treatment of leishmaniasis. To fill this therapeutic gap, several research groups introduced new classes of active compounds against leishmaniasis, including bisindole derivatives. [3]

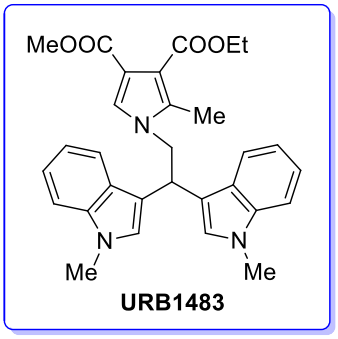

Figure 1

As part of our ongoing investigations on the biological activities and applications of bisindole derivatives [4] and leishmaniasis [3,5], in this contribution, a phenotypic screening of a small library of azole-bisindoles against several human and canine *L. infantum* strains was performed. Most of the tested compounds showed good activity against the promastigotes (IC_{50} values < 10 μM). Among these, **URB1483**, a pyrrole-bisindole derivative (figure 1), showed good activity against intracellular amastigotes, comparable to that of the approved drug pentamidine, and it did not display cytotoxic effects on canine and human cell lines, with a selectivity index > 50. Literature point at *Leishmania* topoisomerase IB as molecular-target for **URB1483** [3] and docking studies support that hypothesis. However, **URB1483** did not inhibit neither human- nor Leishmania-topoisomerase IB in relaxation and cleavage assays. Formulation and preliminary *in vivo* studies will be also presented. Taken together, these data indicate that **URB1483** may represent a promising lead compound for the generation of new anti-*Leishmania* agents with very low toxicity on host cells.

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Development of peptidyl Michael acceptors for S3 pocket investigation of rhodesain, cysteine protease of *Trypanosoma brucei rhodesiense*

Santo Previti,[a] Roberta Ettari,[a] Carla Di Chio,[a] Sandro Cosconati,[b] Giorgio Amendola,[b] Tanja Schirmeister,[c] Maria Zappalà[a]

[a] Department of Chemical, Biological, Pharmaceutical, and Environmental Sciences, University of Messina, Messina 98168, Italy; [b] DiSTABiF, University of Campania Luigi Vanvitelli, Via Vivaldi 43, 81100 Caserta, Italy; [c] Institute of Pharmacy and Biochemistry, University of Mainz, Mainz DE 55128, Germany.

Cysteine proteases are well-known targets for a wide range of diseases [1]. Inhibition of these ubiquitous enzymes leads to the arrest of essential processes for the survival, among other, of parasites, which transmit serious diseases to humans. In the last decades, our research group focused on the development of peptides and peptidomimetics as inhibitors of rhodesain, the main cysteine protease of *Trypanosoma brucei rhodesiense*, the protozoan responsible for Human African Trypanosomiasis [2].

Among all the developed compounds, the most promising inhibitors bear a methyl vinyl ketone warhead (Figure 1), homophenylalanine and phenylalanine residues at the P1 and P2 sites, respectively, and variously decorated aromatic rings at the P3 position [3,4,5]. Considered that K11777, a potent antitrypanosomal agent, bears an ureido group between the P2 and P3 sites, we developed a series of derivatives containing the ureido function between the building peptide fragment Phe-hPhe and the aromatic region at the P3 site.

In parallel to that, with the aim to further explore the characteristics of the S3 pocket, the dipeptide Phe-hPhe was elongated by the introduction of increasing size *N*-Cbz protected amino acids, *i.e.* Gly, Ala, D-Ala, Val, Leu, Cha and Phe.

The synthesis of both series was performed following the standard batch synthetic procedures.

All the molecules were then fully characterized for their inhibitory properties towards rhodesain, and binding affinities (K_i values) in the nanomolar range were observed for most of them. Furthermore, the selectivity against the target protease over human cathepsin L was assessed. The most promising inhibitors have been tested against *T. brucei* infected cells and molecular docking helped us to clarify the binding mode.

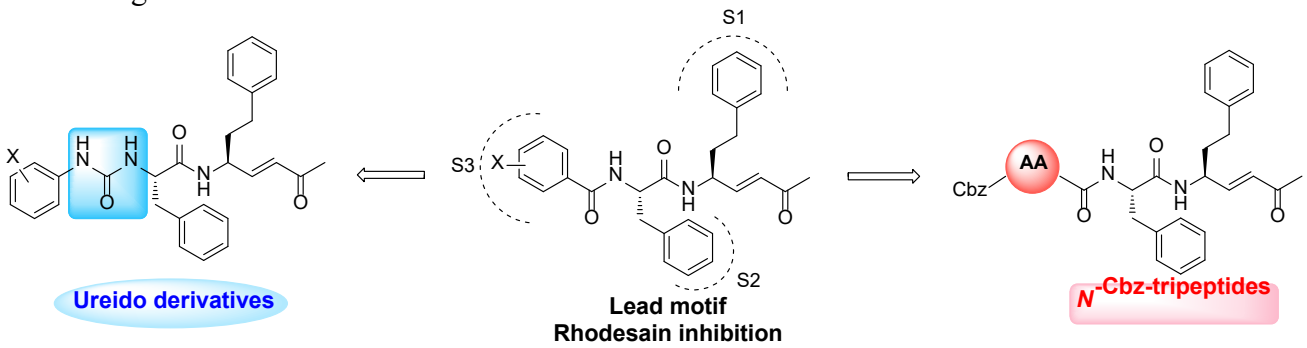

Figure 1. Design of novel Michael acceptors for rhodesain inhibition.

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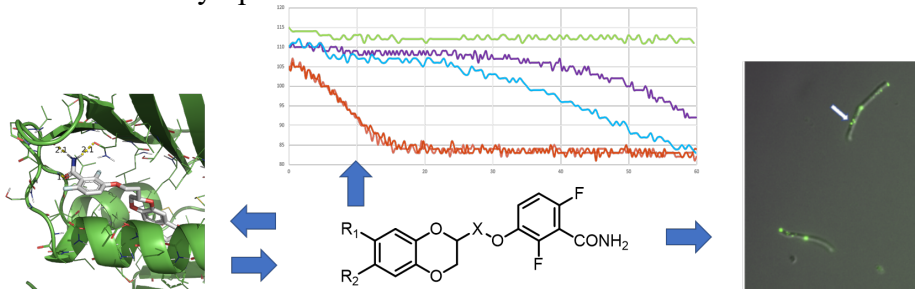
Development of benzodioxane-benzamides inhibitors of FtsZ as potent broad-spectrum antimicrobial agents

Valentina Straniero [a], Lorenzo Suigo [a], Victor Sebastián-Pérez [b,c], William Margolin [d], Marta Sobrinos-Sanguino [b], Carlo Zanotto [e], Begoña Monterroso [b], Martina Hrast [f], Silvia Zorrilla [b], Germán Rivas [b],and Ermanno Valoti [a]

[a] Dipartimento di Scienze Farmaceutiche, Università degli Studi di Milano, 20133 Milano, Italy; [b] Centro de Investigaciones Biológicas Margarita Salas (CSIC), 28040 Madrid, Spain; [c] Exscientia, The Schrödinger Building, Oxford Science Park, UK; [d] Department of Microbiology and Molecular Genetics, McGovern Medical School, University of Texas, Houston, TX 77030, USA; [e] Dipartimento di Biotecnologie Mediche e Medicina Traslazionale, Università degli Studi di Milano, 20129 Milano, Italy; [f] Faculty of Pharmacy, University of Ljubljana, 1000 Ljubljana, Slovenia.

Antimicrobial resistance is a serious worldwide health threat. The identification of novel potential antibiotic targets is one of the ways to slow down its worsening. FtsZ, one of the bacterial cell division machinery proteins, emerged in the last decade for its crucial role in bacterial replication and viability [1]. Benzamide compounds are the most studied and promising FtsZ inhibitors developed so far, due to their high anti-staphylococcal activity, their low cytotoxicity and the interesting results obtained in association with other antibiotic classes [2]. Along these lines, here we report our recent findings on a class of FtsZ inhibitors, containing a 2,6-difluoro-benzamide scaffold linked to a hydrophobically substituted 1,4-benzodioxane ring [3-6]. We firstly validated a robust computational model, which drove us to identify the structural features the 1,4-benzodioxane moiety and the alkoxy linker should possess, in order to perfectly fit the FtsZ binding pocket. We thus developed several interesting compounds, having submicromolar antibacterial activities and showing comparable inhibitory activities towards both Gram-positive (*Staphylococcus aureus* and *Bacillus subtilis*) [3,5] and Gram-negative (*Escherichia coli)* FtsZ. Nevertheless, these derivatives proved to be substrates of *E. coli* efflux pump AcrAB, thus affecting their potencies [4]. These surprising and novel results confirmed how a single molecule can target both species while maintaining potent antimicrobial activity.

We set-up and performed different assays, to firstly validate FtsZ as the target of our class of compounds. Morphometric analysis and fluorescence microscopy let us evaluate the typical alterations of cell division and FtsZ inhibition, as well as the effects on FtsZ localization [6]. Moreover, we took advantages of fluorescence anisotropy to investigate and assess the impact of our derivatives on the kinetics of disassembly of the GTP triggered FtsZ polymers. Furthermore, we used confocal microscopy, to evaluate the shape and the dimension of FtsZ polymers, when in presence or in absence of our compounds in solutions containing crowding agents mimicking the crowded environment in the cytoplasm.



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[6] unpublished data

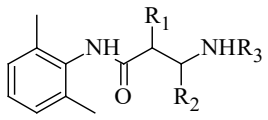
To042: prospective lead compound for the treatment of myotonic syndromes.

Marilena Muraglia,[a] Maria Maddalena Cavalluzzi,[a] Gualtiero Milani,[a] Alessia Carocci,[a] Filomena Corbo,[a] Giovanni Lentini,[a] Antonio Carrieri,[a] Jean F. Desaphy[b] and Carlo Franchini.[a]*

[a]Dipartimento di Farmacia-Scienze del farmaco - Università degli Studi di Bari "A. Moro", via E. Orabona, Bari-Italia; [b]Dipartimento di Scienze biomediche e oncologia - Università degli Studi di Bari "A. Moro" Piazza G. Cesare, Bari-Italia. *marilena.muraglia@uniba.it

In this communication we report the rational design and biological evaluation of Tocainide-related Nav1.4 blockers. These 2,6-xylydides were conceived as potential agents useful for the treatment of excitable tissue disorders, such as skeletal muscle channelopathies, which are generally considered as orphan diseases.[1,2,3]

A large amount of evidence on drug-like properties and selectivity, gave us a clear idea about the structural requirements related to potency and state-dependence of block.



In vitro studies on a wide congeneric series allowed us to identify **To042** as a lead compound in the class of sodium channel blockers, being it effective in the submicromolar range, for the use-dependent block of Nav1.4 channels.[4]

Due to its excellent *in vitro* pharmacodynamic and pharmacokinetic profile and *in vivo* antimyotonic activity, we performed preliminary toxicological studies to obtain data to define a therapeutic index.[5]

By presenting our research findings on this promising molecule, we hope to reach the interest of other research groups, which could cooperate in performing further preclinical and clinical studies on **To042** and possibly pursuing the repositioning strategy.

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Development of mutual prodrugs of 5-fluorouracil and heme oxygenase 1 inhibitor as anticancer agents

Loredana Salerno,[a] Valeriai Ciaffaglione,[a] Luca Vanella,[a] Valeria Sorrenti,[a] Valeria Consoli,[a] Vittorio Canale,[b] Paweł Zajdel,[b] Michela Giuliano,[c] and Sebastiano Intagliata[a]

[a] Department of Drug and Health Sciences, University of Catania, viale A. Doria 6, 95125, Catania, Italy; [b]Department of Organic Chemistry, Jagiellonian University Medical College, 9 Medyczna Str., 30-688, Kraków, Poland; [c] Department of Biological, Chemical and Pharmaceutical Sciences and Technologies (STEBICEF), University of Palermo, Via del Vespro 129, 90127, Palermo, Italy.

The development of multitarget-directed compounds is a medicinal chemistry strategy useful to obtain innovative therapeutics for multifactorial diseases, such as anticancer agents [1]. Although 5-fluorouracil (5-FU) is approved chemotherapy included in the WHO list of essential medicines, its use in the clinic is limited by low drug-like properties and severe side effects [2]. In consequence, the development of prodrugs of 5-FU was envisaged as a rational approach to increase its therapeutic efficacy.

Heme oxygenase 1 (HO-1) is an inducible isoform of a heat shock protein family responsible for the catabolism of heme group. HO-1 is mainly present in the liver and spleen, and importantly it is overexpressed in cancer cells. As a result, high levels of HO-1 in tumor tissues have been correlated to cancer progression, tumor growth, metastasis, and resistance to chemotherapy, even though in a cell line-specific manner. Thus, the pharmacological inhibition of the HO-1 emerged as a promising strategy for mono- and/or adjuvant cancer chemotherapy [3].

Here we present the synthesis of novel 5-FU/HO-1 hybrids designed according to the mutual prodrug approach, in which the two active pro-moieties (i.e., 5-FU and azole-based HO-1 inhibitors) were linked via succinic acid serving as a cleavable linker (Figure 1). Specifically, two different synthetic routes were validated to obtain a key intermediate for future modification as well as to increase the yield of the final products. Subsequent *in vitro* enzymatic stability assessment and preliminary cytotoxicity studies towards selected cancer cell lines (e.g., human prostate, lung, and colon cancer cells) provided promising results which support our strategy. Particularly, newly synthesized 5-FU/HO-1 prodrugs showed a similar effect on cell viability to that produced by the reference drug 5-FU, and lower cytotoxicity on healthy cells than 5-FU. More in-depth studies concerning the mechanism of action of the most potent compound are in progress and will be reported in due course.

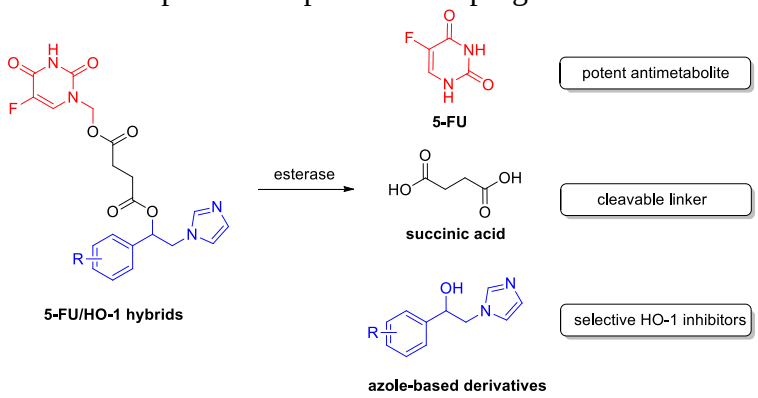

Figure 1. Structural elements of novel 5-FU/HO-1 hybrids.

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LigAdvisor: a web server to perform *in silico* explorations on crystallographic ligands and known drugs for polypharmacology and drug repurposing

Luca Pinzi,[a] Annachiara Tinivella,[a,b] Giulio Rastelli[a]

[a] Department of Life Sciences, University of Modena and Reggio Emilia, Via Giuseppe Campi 103, 41125 Modena, Italy; [b] Clinical and Experimental Medicine, PhD Program, University of Modena and Reggio Emilia, Modena, Italy.

In recent years, polypharmacology and drug repurposing approaches, which are now mainly pursued on rational grounds, have gained increased attention of the research community. Indeed, the design of compounds simultaneously acting on multiple biological targets allow to achieve improved therapeutic effects, compared to single-target and polytherapy approaches [1]. Moreover, the identification of novel uses for approved drugs and clinically assessed candidates can quickly provide innovative treatments towards unmet therapeutic needs [2,3]. Several databases providing medicinal chemistry related data are currently available to facilitate drug repurposing and polypharmacology tasks. However, their information often requires extensive *in silico* processing and integration to be exploited in drug discovery contexts. To help overcoming such limitations, we developed LigAdvisor [4], a web server that integrates information from DrugBank (DB), Protein Data Bank (PDB), UniProt, Therapeutic Target Database (TTD) and clinical trials, with results of chemoinformatic analyses. In particular, chemoinformatic analyses were firstly performed by means of 2D similarity approaches (*i.e.*, MACCS and ECFP4 fingerprints) on ligands extracted from PDB and DB, the curated datasets of molecules being less populated by potential false positive compounds and providing information from the related crystallographic complexes. Then, the results of these analyses were integrated with information related to molecular targets, diseases, and clinical data, retrieved from UniProt, TTD and clinical trials. The generated data was finally framed into a web server to be easily exploited in different drug discovery contexts. LigAdvisor (https://ligadvisor.unimore.it/) is accessible through a user-friendly interface and can be queried both in ligand- and target-based search modes.

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NMR contributions to process chemistry sustainability in the pharmaceutical research area

Lucilla Turco, Andrea Bernardelli, Chiara De Santi, Stefano Provera

Aptuit (Verona) srl, an Evotec Company, Italy

The Green Chemistry concept [1] was firstly introduced in early '90s and can be defined as the "design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances".
Since then, the Green Chemistry has been increasingly used in chemistry and pharmaceutical industries, by application of its twelve principles, which ultimately allow to both decrease the environmental impact and reduce the economic costs.

In this communication we will focus on the eleventh principle of the Green Chemistry [2], which is about real-time analysis for pollution prevention, and show how an analytical technique, such as NMR, can contribute to reduce time, costs and pollution in an early-phase Active Pharmaceutical Ingredient's (API) manufacturing process.

For its low environmental impact and robustness NMR spectroscopy is a useful and low time-consuming technique to monitor scale-up reactions for both qualitative and quantitative purposes. Applications spread from identification of raw materials, intermediates, impurities, APIs to in-process controls.

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A second life for MAO inhibitors: from CNS diseases to cancer

Marco Catto,[1] *Angelina Boccarelli*,[2] *Rosa Purgatorio*,[1] *Mariagrazia Rullo*,[1] *Leonardo Pisani*,[1] *Modesto de Candia*,[1] *Orazio Nicolotti*,[1] *Cosimo D. Altomare*[1]

[1] *Department of Pharmacy-Pharmaceutical Sciences, University of Bari Aldo Moro, via E. Orabona 4, 70125 Bari (Italy);* [2] *Department of Biomedical Sciences and Human Oncology, University of Bari Aldo Moro, Piazza Giulio Cesare 11, 70124 Bari (Italy)*

Monoamine oxidase (MAO) subtypes A and B are the enzymes responsible for the oxidative deamination of amine neurotransmitters. Selective MAO A and B inhibitors are currently used as second-line drugs for the treatment of depression and Parkinson's disease, respectively. MAO inhibitors with additional, multitarget activities are widely studied for their potential in the treatment of neurodegenerative diseases, although to date none still enter clinics. Interestingly, recent studies report on the effectiveness of isoform-selective MAO inhibitors in contrasting chemoresistance and invasiveness of several types of cancers [1], thus suggesting a potential of MAO inhibition in chemotherapy. Particularly, MAO A selective inhibitors proved to be able to overcome the chemoresistance of highly recurrent prostate cancer (PC) [2], and indeed the MAO A irreversible inhibitor phenelzine is currently under clinical investigation in non-metastatic recurrent PC [3]. Other evidences suggest an antiproliferative effect in other types of cancer, possibly related to the drop of oxidative stress induced by MAO inhibition [4].

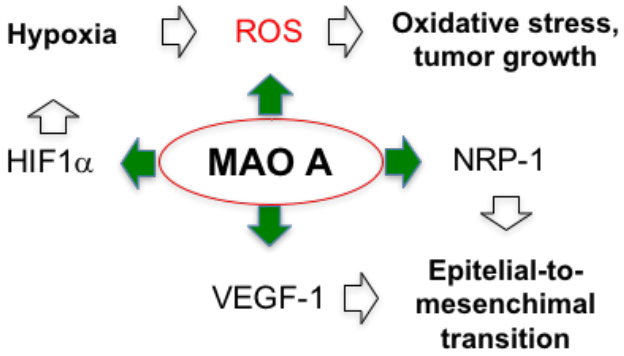

Figure 1. Possible roles of MAO A in tumor proliferation.

Based on our long-standing experience in the discovery of potent and selective MAO A/B inhibitors [5], we are currently investigating a possible antiproliferative activity of coumarin-based MAO A selective inhibitors in MCF-7 and MDA-MB231 breast cancer cells. The first outcome of this study will be presented, either in terms of intrinsic cytostatic activity or in light of possible synergistic effects in co-administration with known anticancer drugs and in other antiproliferative features, like the inhibition of tumor cell migration, a known MAO-mediated tumorigenic event (Fig. 1).

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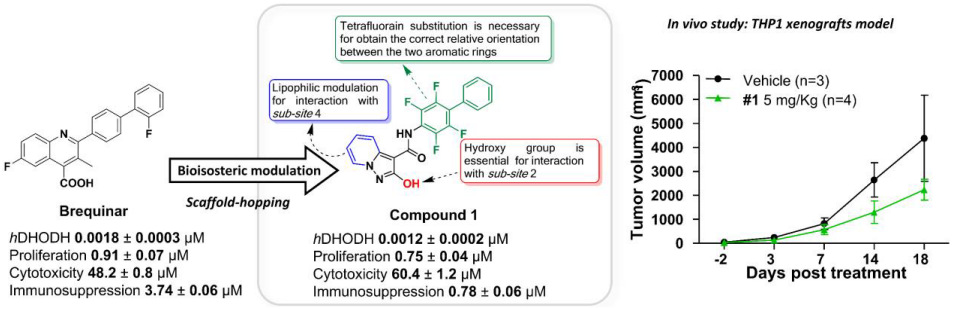
Apoptotic and differentiating therapy for AML using potent human dihydroorotate dehydrogenase inhibitor

Sainas S.[a], Circosta P.[b], Pippione A. C.[a], Giorgis M.[a], Marraudino M.[c], Houshmand M.[b], Bonaldo B.[c], Gaidano V.[b], Cignetti A.[b], Saglio G.[b], Al-Karadaghi S.[d], Boschi D.[a] and Lolli M.L.[a]

[a]Department of Science and Drug Technology, University of Torino (Italy); [b]Department of Clinical and Biological Sciences, University of Torino (Italy); [c]Neuroscience Institute Cavalieri Ottolenghi, Department of Neuroscience Rita Levi Montalcini, University of Torino, (Italy); [d]Department of Biochemistry and Structural Biology, Lund University (Sweden);

In acute myeloid leukemia (AML), blasts lose their ability to differentiate into mature cells and undergo apoptosis. Accordingly, a proapoptotic and differentiating therapy (arsenic and all trans retinoic acid, ATRA) has dramatically improved survival in acute promyelocytic leukemia; however, such combination therapy is not available for other AML subtypes. While, in 2016, inhibition of dihydroorotate dehydrogenase (DHODH), a key enzyme of the pyrimidine biosynthesis, was found to induce differentiation in several AML models. In fact, brequinar (BRQ) was utilized in vivo studies.[1] We are optimizing *h*DHODH inhibitors to improve potency and drug-like proprieties. The main objective is to identify the best inhibitor suitable for use in *in vivo* studies on AML animal model.

In this work we will present a new generation of *h*DHODH inhibitors able to reach the enzymatic BRQ inhibition potency levels. Our data showed that compound **1**, the best of two series, induced apoptosis in multiple AML cell lines, not only because of differentiation, but also directly. Its combination with antileukemic agents further increased the apoptotic rate, but when experiments were performed in the presence of physiological uridine concentrations, results were less impressive. Conversely, the combination of compound **1** with dipyridamole induced metabolic lethality and differentiation in all AML cell lines; this extraordinary synergism was confirmed on AML primary cells with different genetic backgrounds and was unaffected by physiological uridine concentrations, predicting in human activity. [2,3,4] Finally, our preliminary results from *in vivo* experiments showed that *i*) compound **1** wasn't toxic on Balb/c mice after 5 weeks of intraperitoneal administration at two different doses 10 and 25 mg/Kg and during acute toxicity experiment was not toxic ad dose of 1 g/Kg; *ii*) the half-life was limited to 3-4 hours and *iii*) compound **1** had a good antileukemic activity (approximately 50% reduction of the tumour volume compared with control, after 18 days of treatment in THP1-xenograft models obtained from NSG mice). Theoretical design, modelling, synthesis, SAR, X-ray crystallographic data, biological assays, Drug-Like proprieties, pharmacokinetic studies, and in vivo evaluations on AML models will be here presented and discussed.



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Constrained 1,4-Dialkylpiperazines as Dopamine Transporter (DAT) Inhibitors to Fight Psychosis and Cocaine Addiction

Claudia Sorbi [a], *Pasquale Linciano* [a], *Antonietta Vilella* [b], *Eleonora Daini* [b], *Massimo Grilli* [c], *Giulia Vallarino* [c], *Theresa Kopajtic* [d], *Mike Michaelides* [d], *Jonathan L. Katz* [d], *Michele Zoli* [b], *Livio Brasili* [a], *and Silvia Franchini* [a]

[a]*Department of Life Science, University of Modena and Reggio Emilia, Modena, Italy*
[b]*Centre for Neuroscience and Neurotechnology, University of Modena and Reggio Emilia, Modena, Italy*
[c]*Department of Pharmacy (DIFAR), University of Genoa, Genoa, Italy*
[d]*Psychobiology Section, Molecular Neuropsychiatry Branch, National Institute on Drug Abuse, Baltimore, MD, USA*

Dysregulation of dopaminergic neurotransmission plays a role in the pathology of several diseases and conditions such as schizophrenia, depression, ADHD (Attention-Deficit/Hyperactivity Disorder), Parkinson's as well as drug addiction. Although D_2 receptor antagonists are effective in the management of psychosis, their chronic treatment is always associated with extrapyramidal side effects and increased prolactin levels. Over the last decades, a number of antipsychotics have appeared but only limited progress has been made in the search of novel compounds with a new mechanism of action. In addition to the D_2 receptor blockade, an innovative approach could be represented by the modulation of the extracellular levels of dopamine (DA), i.e. by acting on the DA reuptake. The advantage of this "presynaptic approach" is that only spontaneously active synapses will be affected by the dopamine transporter (DAT) inhibitor, thus limiting the extrapyramidal side effects. Drug addiction is also a serious health and societal problem and no approved therapeutics have been obtained so far. Vanoxerine (GBR12909), an atypical DAT inhibitor, dropped out of Phase I clinical trials for Cocaine abuse, due to cardiotoxicity issues.
In the search for potent and safer DAT inhibitors our research group synthesized and tested a series of constrained analogues of vanoxerine named DAhLIs (DAT AtypicaL Inhibitors). While the phenylpropylpiperazine and the fluoro-phenyl moieties were maintained unaltered, the ethyl ether linker of vanoxerine was frozen in a tetrahydrofuran, dioxolane, dioxane, oxathiolane and dithiolane ring. Since cyclization introduces one chiral center, the enantiomeric couples were prepared following enantioselective synthesis. DAhLIs were tested for the affinity at DA, Serotonin (SERT) and Noradrenaline (NET) Transporters showing DAT low nanomolar affinity and selectivity. The compounds were also evaluated for the affinity on human voltage-gated potassium ion channel (hERG) showing lower cardiotoxicity compared to Vanoxerine. The most promising compounds were tested *in vivo* in C57BL6J wild type mice. Preliminary results showed that DAhLIs: i) have putative central effects, ii) unlike Vanoxerine, reduce novelty-induced locomotor activity, and iii) counteract Cocaine stimulating effects, suggesting that they modulate DA reuptake via DAT. To shed light on DAhLIs' mechanism of action, microdialysis experiments were performed. Perfusate levels of DA were detected by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) after administration or co-administration of DAhLI or/and Cocaine. Pharmacokinetic studies are currently ongoing and the results will be presented in due course. In conclusion, our findings unveil a new promising class of 1,4-dialkylpiperazines as potential presynaptic antipsychotics or tool compounds for cocaine abuse.

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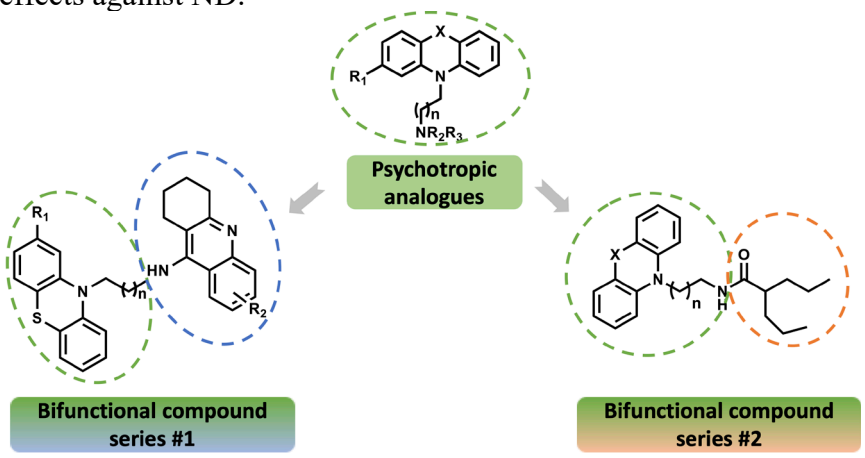
Psychotropic-based bifunctional compounds for neurodegenerative diseases

*Elisa Uliassi[a], Francesca Massenzio[a], Angela De Simone[b], Vincenza Andrisano[c], Barbara Monti[a], Maria Laura Bolognesi[a,]**

[a] *Department of Pharmacy and Biotechnology, University of Bologna, 40126 Bologna, Italy;* [b] *Department of Drug Science and Technology, University of Torino, 10125 Torino, Italy;* [c] *Department for Life Quality Studies, University of Bologna, 47921 Rimini, Italy.*

Neurodegenerative diseases (ND) have grown as a leading biomedical and societal challenge. The current lack of effective treatments for ND is likely due to their multifactorial etiology, which calls for innovative drug discovery approaches. Bifunctional compounds, consisting of two protein-binding moieties able to interact with two targets simultaneously, have great potential to address the multifactorial and complex nature of ND and may provide effective therapies.
In our previous efforts, we further validated the tricyclic arylalkylamine structure, not only for the well-known psychotropic effects, but as a privileged chemotype against neurodegeneration [1]. We report herein on the development of psychotropic-based bifunctional small molecules for ND, in which this chemotype has been combined with a second protein-binding moiety.
As first series, we developed a 36-memberd library of phenothiazine-based bifunctional compounds for Alzheimer's disease [2]. In particular, these have been rationally designed by linking differently substituted phenothiazines, which possess neuroprotective and antiaggregating effects, to the anticholinesterase activity of tacrine derivatives via a methylene spacer of varying length. The resulting bifunctional compounds displayed anticholinesterase, anti-tau and anti-amyloid properties together with a good safety and pharmacokinetic profile [2], thus supporting our rationale.
In a second series of seven bifunctional compounds, we joined the structural features of selected psychotropic analogues with valproic acid (VPA) [3]. Our strategy was founded upon the reported beneficial effects of VPA in various ND models, as its epigenetic action is accompanied by a wide range of neuroprotective and neuroregenerative effects. Thus, the primary amines of selected tricyclic psychotropic analogues were combined to the carboxylic function of VPA through an amide bond to generate bifunctional small molecules, potentially endowed with multiple neuroprotective effects against ND.



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[3] unpublished results.

Identification of carbapenemase broad-spectrum inhibitors through *in silico* methodologies

Francesca Spyrakis [1], Donatella Tondi [2], Eleonora Gianquinto [1], MariaCristina Failla [1], Loretta Lazzarato [1], Pasquale Linciano [2], Matteo Santucci [2], Lorenzo Maso [3], Simon Cross [4], Filomena Sannio [5], Federica Verdirosa [5], Filomena De Luca [5], Jean-Denis Docquier [5], Laura Cendron [3], Alberto Venturelli [2], Gabriele Cruciani [6], Maria Paola Costi [2]

[1]Dept. of Drug Science and Technology, University of Turin, Italy. [2]Dept. of Life Sciences, University of Modena and Reggio Emilia, Italy. [3]Dept. of Biology, University of Padua, Italy. [4]Molecular Discovery Ltd, UK. [5]Dept. of Medical Biotechnology, University of Siena, Italy. [6]Dept. of Chemistry, Biology and Biotechnology, University of Perugia, Italy.

The ongoing emergence of bacterial strains resistant to even third- and fourth-generation β-lactam antibiotics is one of the most pressing and challenging issues in clinical therapy. Resistance is most often mediated by β-lactamases (BLs), and in particular by carbapenemases (i.e. KPC, NDM-1, VIM), which have emerged in both Gram-positive and Gram-negative bacteria. Among these, NDM-1 is recognized as a global health threat, capable of easy propagation to other species. Here we applied a multidisciplinary approach integrating *in silico/in vitro* analysis for the design and identification of novel non-covalent BL inhibitors. We performed a parallel screening of commercially available compounds towards a panel of clinically relevant BLs: class A CTX-M-15 and KPC-2, class B NDM-1 and VIM-2, and class C AmpC, and we identified preferred scaffolds for many of these targets. While all BLs seem to prefer, in general, electron donor scaffolds, KPC-2 is preferentially inhibited by sulfonamide and tetrazole-based compounds, NDM-1 by compounds bearing a thiol or a thioureidic moiety, and VIM-2 by triazole-based molecules. These finding may help the design and optimization of inhibitors able to target a specific type of BL and have been supported by crystallographic structures of NDM-1 and VIM-2 complexed with two promising inhibitors. More interestingly, some compounds demonstrated to have a broad-spectrum profile towards both class A and class B representatives and showed to potentiate antibiotic activity towards carbapenemase-producing clinical strains [1]. Interestingly, compound 40 was able to reduce the MIC of imipenem from 16 to 1 μg/mL in an NDM-1 producing clinical isolate, being below the resistance breakpoint as defined by both CLSI and EUCAST.
Parallelly, we have selected the 4-amino-1,2,4-triazole-3-thione as the starting scaffold for the design and synthesis of a small library of new possible MBL inhibitors. The compounds in the library were designed to extend their activity towards class A SBL KPC-2, while maintaining the inhibition towards MBLs. The broad-spectrum profile of the obtained derivatives was validated *in vitro* against one SBL representative, class A carbapenemases KPC-2, and against two representatives of the MBLs subclass B1, VIM-1 and IMP-1.
The compounds thus identified represent novel drug-like leads with valuable biological activity to be directed to hit-to-lead development.

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1,2,4-Triazolo[1,5-*a*]pyrimidines: efficient one-step synthesis and functionalization as antiviral agents

Tommaso Felicetti,[a] Maria Chiara Pismataro,[a] Chiara Bertagnin,[b] Martina Pacetti,[a] Anna Bonomini,[b] Violetta Cecchetti,[a] Arianna Loregian,[b] Oriana Tabarrini,[a] and Serena Massari[a]

[a] *Department of Pharmaceutical Sciences, University of Perugia, Via Del Liceo 1, 06123, Perugia, Italy*
[b]*Department of Molecular Medicine, University of Padua, Via Gabelli 63, 35121 Padua, Italy*
serena.massari@unipg.it

[1,2,4]Triazolo[1,5-*a*]pyrimidine (TZP) is a privileged structure that has been even more used in recent years in the development of antiviral agents [1]. In the search for new anti-influenza (flu) virus compounds, we exploited the TZP core to obtain compounds endowed with the ability to disrupt flu RNA-dependent RNA polymerase (RdRP) PA-PB1 subunits heterodimerization [2].
In the development of novel anti-flu TZPs, we initially focused on the TZP chemistry, by developing efficient one-step procedures for the regioselective synthesis of differently functionalized TZPs. Accordingly, herein, we report the best conditions for the synthesis of TZPs reacting 3,5-diamino-1,2,4-triazole or ethyl 5-amino-1,2,4-triazole-3-carboxylate with ambident electrophiles such as β-diketones, α,β-enones, β-enaminones, β-amino ketones and β-ketoesters, thus experimentally determining their reactivity [3].
In addition, based on previous SAR information, we properly functionalized the scaffolds synthesized to give a set of TZP derivatives that was evaluated for their anti-flu activity. For the best compounds able to significantly disrupt PA-PB1 association and inhibit viral replication [3,4], in depth studies were performed to determine their ability to interfere with RdRP functions, the metabolic stability, and the predicted binding mode within the PA_C cavity. Further studies (i.e., solubility evaluation, LogD assessment and X-ray structure determination) were also performed for a couple of regioisomers, in order to investigate how much physicochemical properties can impact PA-PB1 interaction and viral growth inhibitions.
Finally, a selection of TZPs was also tested against SARS-CoV-2, leading to the identification of some active compounds, with the most promising compound from this series displaying an EC_{50} value of 34.47 μM, highlighting the potential of the TPZ scaffold in the search for anti-CoV agents.

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An integrated metabolomic and proteomic approach for the identification of covalent inhibitors of the main protease (M^{pro}) of SARS-COV-2 from crude natural extracts

Altomare, A.;[a] *Baron G.;*[a] *Ferrario G.;*[a] *Carini M.;*[a] *Bombardelli E.;*[b] *and Aldini, G.*[a]

[a]*Department of Pharmaceutical Sciences, University of Milan, Via Mangiagalli 25, Milan, Italy;* [b]*Plantexresearch Srl, Milan, Italy;*

The viral 3CL protease of SARS-CoV-2, also called the main protease (M^{pro}) is a chymotrypsin-like protease which plays an essential role in coronavirus replication by digesting the viral polyproteins; it is considered one of the key antiviral drug targets thus laying a solid background for the development of M^{pro} inhibitors as SARS-CoV-2 antivirals. [1-3] Virtual screening campaigns and HTS tests have identified several natural compounds as M^{pro} inhibitors, indicating that plants are a valuable source of bioactive compounds. Most of the virtual and *in vitro* methods used to screen M^{pro} natural inhibitors are based on databases and chemical libraries, hence based on structurally elucidated and isolated derivatives. We believe that a method able to fish out bioactive compounds from crude extracts, containing unknown components, not available in chemical libraries, would extend our current knowledge. However, the search for bioactive compounds from a complex crude mixture is quite challenging and requires an analytical method able to identify compounds through an untargeted approach. The aim of the study was to set-up a high resolution mass spectrometry (HRMS) platform able to fish out covalent inhibitors of M^{pro} from complex natural extracts. The study was firstly based on a metabolomic approach consisting of profiling the extracts, by annotating the unknown compounds and their MW. The second step was based on identifying those natural electrophilic compounds able to form a Michael adduct with thiols, a peculiar chemical feature of many M^{pro} inhibitors that covalently bind the catalytic Cys145 in the active site, thus stabilizing the complex [1]; even very mild electrophilic species could be identified by incubating natural extracts with free thiols (cysteine and cysteamine) at pH 8, thus favoring the reactive form thiolate. In this perspective, a HPLC-MS method, operating in neutral loss scan mode, was optimized and applied to assign the MW values to the electrophilic species forming Michael adducts with thiols, an information used in the following step. The final stage consisted of incubating recombinant M^{pro} with the natural extracts and identifying the compounds adducted to the catalytic Cys145 by means of a bottom-up proteomics analysis based on a nano-LC-HRMS method (Orbitrap ELITE, Thermo). Data analysis was based on two complementary strategies: (i) a targeted searching was applied by setting the moieties identified in the second step, namely covalent Cys/cysteamine adducts, as variable modifications; (ii) an untargeted approach was used to identify the whole range of adducted peptides containing Cys145 (M^{pro}) on the basis of the characteristic *y* and *b* fragment ions of the peptide. The selectivity of compounds towards Cys145 of M^{pro}, as a result of a specific engagement with the binding site was measured by evaluating their ability to covalently bind the free Cys34 of HSA (bottom-up / top-down approaches). The study was validated by testing non-peptidomimetic inhibitors of M^{pro}, namely baicalin / baicalein and myricetin, that exhibited potent antiviral activities in cell-based systems [4,5]. We believe that the proposed HRMS method can be generally applied to fish out bioactive compounds from complex mixtures toward target proteins whose protein-ligand engagements involve a covalent binding.

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Discovery of non-DKA derivatives endowed of selective activity against ribonuclease H function of the HIV-1 reverse transcriptase

Antonella Messore,[a] Valentina Noemi Madia,[a] Francesco Saccoliti,[b] Valeria Tudino,[a] Alessandro De Leo,[a] Davide Ialongo,[a] Luigi Scipione,[a] Daniela De Vita,[c] Sandro Cosconati,[d] Mathieu Métifiot,[e] Enzo Tramontano,[f] Roberto Di Santo,[a] and Roberta Costi[a]

[a] Dipartimento di Chimica e Tecnologie del Farmaco, Istituto Pasteur-Fondazione Cenci Bolognetti, "Sapienza" Università di Roma, p.le Aldo Moro 5, I-00185, Rome
[b] D3 PharmaChemistry, Italian Institute of Technology, Via Morego 30, I-16163 Genova
[c] Department of Environmental Biology, "Sapienza" University of Rome, p.le Aldo Moro 5, I-00185, Rome
[d] DiSTABiF, University of Campania "Luigi Vanvitelli", Via Vivaldi 43, 81100 Caserta, Italy
[e] CNRS - Université de Bordeaux, 146 rue Léo Saignat, 33076, Bordeaux cedex, France
[f] Department of Life and Environmental Sciences, University of Cagliari, Cittadella Universitaria di Monserrato, SS554 -09042 Monserrato (CA), Italy

The conversion of the viral RNA into DNA is a critical step in the HIV-1 life cycle initiated by the reverse transcriptase (RT), a well-established drug target. RT is a multifunctional enzyme with RNA and DNA-dependent DNA polymerase (RDDP and DDDP respectively), and ribonuclease H (RNase H) activities. RNase H function is essential for virus replication since it specifically cleaves the RNA moiety of RNA/DNA hybrid to generate a DNA duplex to be integrated into the host cell. The RNase H active site contains a highly conserved DEDD motif consisting of four carboxylate amino acid residues in close proximity (D443, E478, D498, and D549) that interact with two Mg^{2+} ions [1].

Despite being a valid and promising drug target, RNase H inhibitors have not reached the clinical pipeline yet. Indeed, all the RT-targeting drugs approved so far are inhibitors of the RDDP activity and the development of RNase H inhibitors (RHIs) has lagged behind so that no drug targeting RNase H has been approved yet. This can be attributed to: i) the availability of expertise on inhibitors of other DNA polymerases that encouraged the development of drugs targeting the RT-RDDP function, and ii) the open morphology of the RNase H function hard to target, and showing a strong competition with the substrate for the access to the catalytic core [1]. Recently we described a dual activity of DKA derivatives as inhibitors of both integrase and RNase H function of RT [2-3]. Herein we describe the application of an isosteric approach to convert these metabolically unstable DKA to more drug-like scaffolds [4]. This approach has been successful and also led to inhibitors that selectively target RNase H function vs IN enzyme.

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Peptides from bench to clinical studies: our experience with CXCR4

Salvatore Di Maro,[a] Stefano Tomassi,[b] Anna Maria Trotta,[c] Luigi Portella,[c] Stefania Scala,[c] Luciana Marinelli,[b] Ettore Novellino,[b]

[ac]DiSTABiF, Università della Campania "Luigi Vanvitelli", 81100 Caserta, Italy; [b]Dipartimento di Farmacia, Università di Napoli Federico II, 80131, Naples, Italy; [c]Molecular Immunology and Immunoregulation, Istituto Nazionale Tumori "Fondazione G. Pascale", IRCCS-Napoli, 80131 Naples, Italy;

Among the different signaling pathways directly and indirectly involved in cancer immune-resistance and migration, the C-X-C motif chemokine 12 (CXCL12), also known as SDF-1 alpha (stromal-cell derived factor-1alpha), and its receptor CXCR4 have been extensively investigated for their contribution in both tumor growth and metastasis.[1] With the aim to discover novel CXCR4 antagonists suitable for anticancer therapy, we previously identified a CXCL12-derived small cyclic peptide, that bound the CXCR4 in the μM regimen.[2] Despite its promising in-vitro activity, this peptide suffered of two main drawbacks, which hampered any further biological evaluation: a) low metabolic stability in biological fluids; b) unsuitable potency for *in-vitro* to *in-vivo* translation in preclinical model. Herein, we embarked into an extensive lead optimization campaign to enhance both the metabolic stability and the target affinity. A preliminary in vitro metabolic assessment of the peptide was performed in human serum to identify its main proteolytic sites, providing the rationale for setting a strategy of modifications, including N- and C-terminal modification, D-amino acid scan, Ala-scan and amino acid replacement. Some of the obtained analogues exhibited longer *in vitro* half-life as well as a dramatic enhancement of affinity for CXCR4 with the respect to the parent peptide.[3-5] In-depth biological characterization revealed its selectivity versus other related and unrelated chemokine receptors, its ability to block CXCL12-dependent cell migration and CXCL12-mediated CXCR4 internalization, which are validated hallmarks for CXCR4 antagonism.[4-5]These encouraging results set the stage for the successive study aimed at converting our potent and selective CXCR4 antagonist in a potential radiolabeled probe to *in-vivo* detect pertinent tumors. Several linkers were introduced at different positions within the sequence to identify the peptide region that could be functionalized with chelating moieties for ^{68}Ga, without significantly affecting the affinity for the receptor. Finally, the [^{68}Ga]NOTA and [^{68}Ga]DOTA analogues were employed for the *in vivo* PET imaging studies using CHO-hCXCR4 and Daudi lymphoma cells, revealing higher CXCR4-specific tumor uptake and high tumor/background ratios for the [^{68}Ga]NOTA than for the [68Ga]DOTA analogue in both *in vivo* models.[6]

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A novel β-hairpin peptide derived from the ARC repressor selectively interacts with the major groove of B-DNA

Azzurra Stefanucci,[1,] Jussara Amato,[2] Diego Brancaccio,[2] Bruno Pagano,[2] Antonio Randazzo,[2] Federica Santoro,[2] Laura Mayol,[2] Soraya Learte-Aymamí,[3] Jessica Rodriguez,[3] José Luis Mascareñas,[3] Ettore Novellino,[2] Alfonso Carotenuto,[2] Adriano Mollica[1]*

[1] *Department of Pharmacy, University of Chieti-Pescara "G. d'Annunzio", Via dei Vestini 31, 66100 Chieti, Italy.*
[2] *Department of Pharmacy, University of Napoli "Federico II", Via Montesano 49, 80131 Naples, Italy.*
[3] *Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), and Departamento de Química Orgánica. Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.*

a.stefanucci@unich.it

Transcription factors (TFs) have a remarkable role in the homeostasis of the organisms and there is a growing interest in how they recognize and interact with specific DNA sequences. TFs recognize DNA using a variety of structural motifs. Among those, the ribbon-helix-helix (RHH) proteins, exemplified by the MetJ and ARC repressors, form dimers that insert antiparallel β-sheets into the major groove of DNA. A great chemical challenge consists of using the principles of DNA recognition by TFs to design minimized peptides that maintain the DNA affinity and specificity characteristics of the natural counterparts. In this context, a peptide mimic of an antiparallel β-sheet is very attractive since it can be obtained by a single peptide chain folding in a β-hairpin structure and can be as short as 14 amino acids or less [1].
Herein, we designed eight linear and two cyclic dodeca-peptides endowed with β-hairpins. Their DNA binding properties have been investigated using fluorescence spectroscopy together with the conformational analysis through circular dichroism and solution NMR. Peptide **6** is able to bind DNA, albeit without sequence selectivity. Notably, it shows a topological selectivity for the major groove of the DNA which is the interaction site of ARC and many other DNA-binding proteins. Moreover, we found that a type I' β-hairpin folding pattern is a favorite peptide structure for interaction with the B-DNA major groove [2].
Peptide **6** is a valuable lead compound for the development of novel analogs with sequence selectivity.

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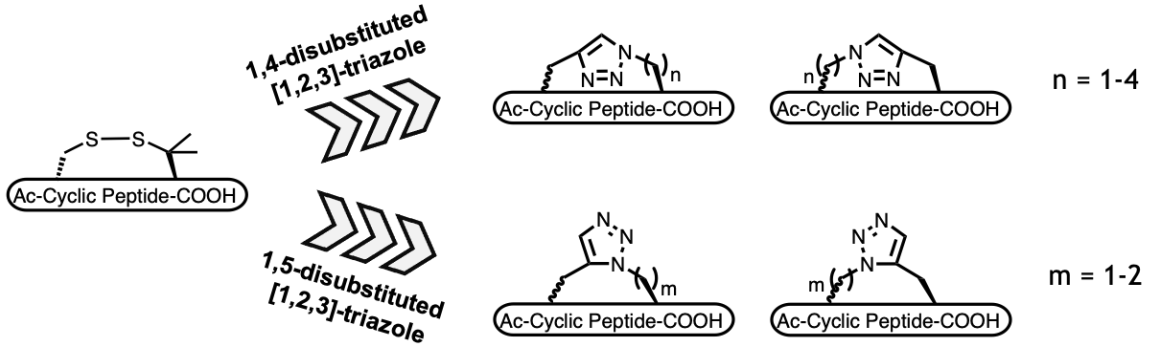
Shading the activity of a CXCR4-interacting peptide by 1,4- and 1,5-disubstituted [1,2,3]-triazole-based cyclization

Stefano Tomassi,[a] Annamaria Trotta,[b] Ettore Novellino,[a] Luciana Marinelli,[a] Stefania Scala,[b] Salvatore Di Maro [c]

[a]Dipartimento di Farmacia, Università di Napoli Federico II, 80131, Naples, Italy; [b]Molecular Immunology and Immunoregulation, Istituto Nazionale Tumori "Fondazione G. Pascale", IRCCS-Napoli, 80131 Naples, Italy; [c]DiSTABiF, Università della Campania "Luigi Vanvitelli", 81100 Caserta, Italy

Disulfide bond is a post-translational modification occurring on cysteine sulfhydryl groups of proteins and is widely employed for stabilizing the conformation of biologically relevant cyclic peptides. However, it is susceptible of redox and metabolic instability and synthetic limitations. Among the disulfide bond bio-isosteres, the [1,2,3]-triazolyl linkage gained considerable interest due to its synthetic orthogonality and stability, although its applicability has proved on limited biological systems. To investigate the effects of the disulfide-triazole replacement on the modulation of G-protein coupled receptor family, we selected a cyclo-heptapeptide (Ac-Arg-Ala-[cys-Arg-2Nal-His-Pen]-COOH), acting as selective chemokine receptor 4 (CXCR4) antagonist.[1,2] Its disulfide bridge was replaced with 1,4- and 1,5-disubstituted [1,2,3]-triazolyl moieties obtained by Cu- and Ru-catalized Alkyne-Azide Cycloaddition on ω-alkynyl and ω-azido amino acids with different configuration and side chain length. Being an asymmetric linkage, the orientation of the triazolic cyclization relative to the amide backbone was also investigated. These structural features were correlated with *in vitro* activity on CEM-CCRF human T leukemia cells overexpressing CXCR4 and most potent compounds assessed for selectivity over closely related chemokine receptors. Noteworthy, functional assay revealed an unpredicted shift to agonistic behavior in cell migration experiments that was rationalized by conformational analysis.[3] This study unveiled that 1,4- and 1,5-disubstituted [1,2,3]-triazoles should not considered as simple bio-isosteres but rather as valuable tools to finely tune the functional profile of GPCR-interacting cyclic peptides.



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GRAFTING TEMPORIN L PEPTIDES: OLD TACTICS FOR NEW ANTIMICROBIAL WEAPONS

R. Bellavita,[a] B. Casciaro,[b] M.L. Mangoni,[c] S. Galdiero,[a] P. Grieco,[a] F. Merlino.[a]

[a]Department of Pharmacy, University of Naples, 'Federico II', Via D. Montesano 49, 80131, Naples, Italy; [b]Center for Life Nano Science@Sapienza, Italian Institute of Technology, Rome, Italy; [c]Department of Biochemical Sciences 'A. Rossi Fanelli', Istituto Pasteur-Fondazione Cenci Bolognetti, Sapienza University of Rome, Rome, Italy.

Antimicrobial peptides (AMPs) represent a valid chance to overcome and control the antibiotic resistance, since they act by a different mechanism of action from conventional antibiotics. Among AMPs the frog skin temporins are encouraging candidates in the development of novel antimicrobial agents.[1] Previous solution state NMR studies revealed that Temporin L shows a high helical content (>70%) responsible for its strong hemolytic activity, correlated to a "barrel stave" mechanism.[2] Moreover, it displays an helical structure at C-terminus in SDS micelles which is crucial for its antibacterial activity.[3]

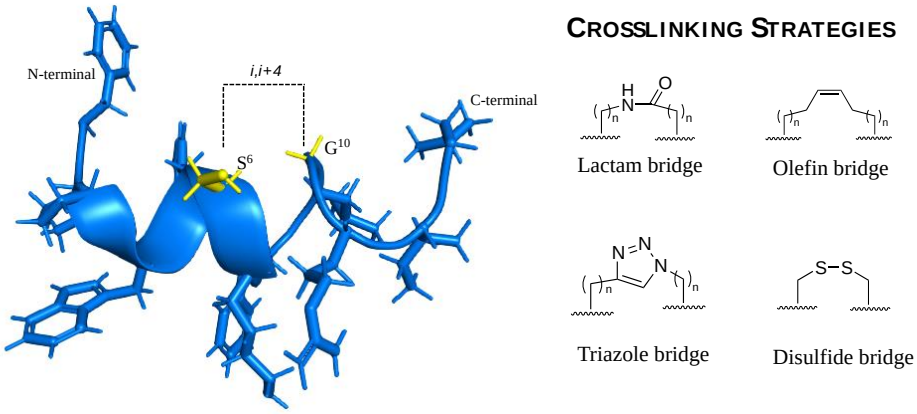

Figure 1. Crosslinking strategies in different *i,i+4* positions of [Pro^3,DLeu^9]TL analogue used in our studies.

Herein, we designed a library of constrained α-helical macrocyclics of non-cytotoxic Temporin L analogue, named [Pro^3,DLeu^9]TL, by incorporation of lactam, triazole, hydrocarbon, and disulfide bridge in different positions *i,i+4* (Figure 1), in order to stabilize the helical conformation at the C-terminus and to investigate the impact of α-helical content on antimicrobial activity, but preserving a low hemolytic activity. The antimicrobial activities of all compounds were evaluated both on Gram-positive and Gram-negative strains, while the cytotoxicity and antibiofilm activities were evaluated only for the most active compounds. Helical contents of the most promising peptides were predicted by using CD spectra in different environments (water, SDS and liposomes). The mechanism of action was investigated by performing fluorescence assays, specifically Leakage, Laurdan and Thioflavin T assays, and finally the proteases stability, due to the structural constrains, was assessed during human serum biostability assay.

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Modulators of Coactivator-Associated Arginine Methyltransferase 1 (CARM-1): There and Back Again

Milite, C.,[a] *Feoli, A.,*[a] *Iannelli, G.,*[a] *Castellano, S.*[a] *and Sbardella, G.*[a]

Department of Pharmacy, Epigenetic Med Chem Lab, University of Salerno, via Giovanni Paolo II 132, I-84084 Fisciano, SA, Italy.

The methylation of arginine residues is a post-translational modification found in both nuclear and cytoplasmic proteins, which are involved in several different cellular processes, including transcriptional regulation, RNA metabolism, and DNA damage repair. Enzymes of the protein arginine *N*-methyltransferase (PRMT) family catalyse the transfer of a methyl group from the donor *S*-adenosyl-*l*-methionine (SAM or AdoMet) to the guanidinium side chain of arginine residues in the target protein. A few years ago, starting from **AMI-1** (the first inhibitor of PRMTs) [1] we identified **EML108**, which was characterized by an improved selectivity profile among methyltransferases and a good cellular activity.[2] Later, pursuing our efforts toward the identification of potent and selective PRMTs inhibitors, we replaced the hydroxynaphthalene moiety with the bioisosteric indole framework. Surprisingly, instead of new PRMT inhibitors, we identified a new class of CARM-1 activator able to increase the methylation of histone (H3) or nonhistone (PABP1) substrates both in in vitro and in cellular models. [3] Therefore, we moved back to our original scaffold **EML108** and, applying a multisubstrate adduct approach, we designed some new ligands of PRMTs. Firstly, we prepared some derivatives bearing a guanidine moiety connected to the naphthalene scaffold *via* a variable linker, then the scaffold was further functionalized with an adenosine moiety (Figure 1). With this multi-substrate-adduct approach we were able to identify new nanomolar selective inhibitors of the arginine methyltransferase CARM-1.

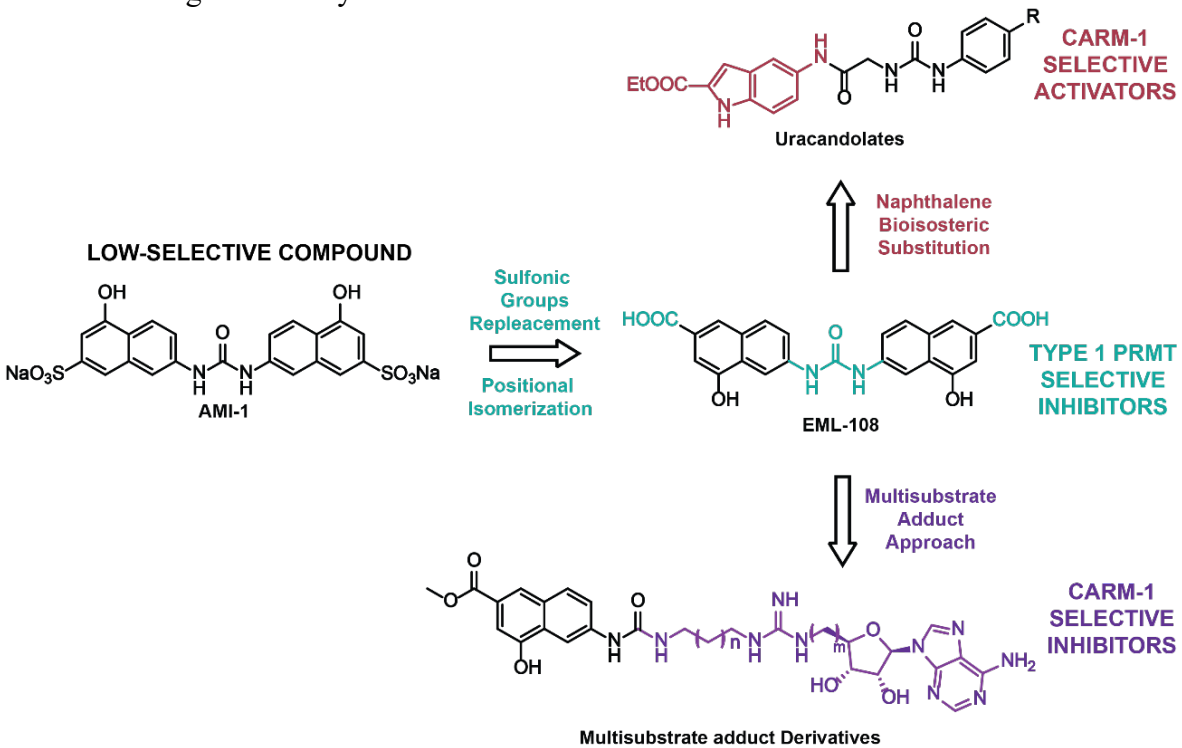

Figure 1. Approaches for the identification of CARM-1 modulators.

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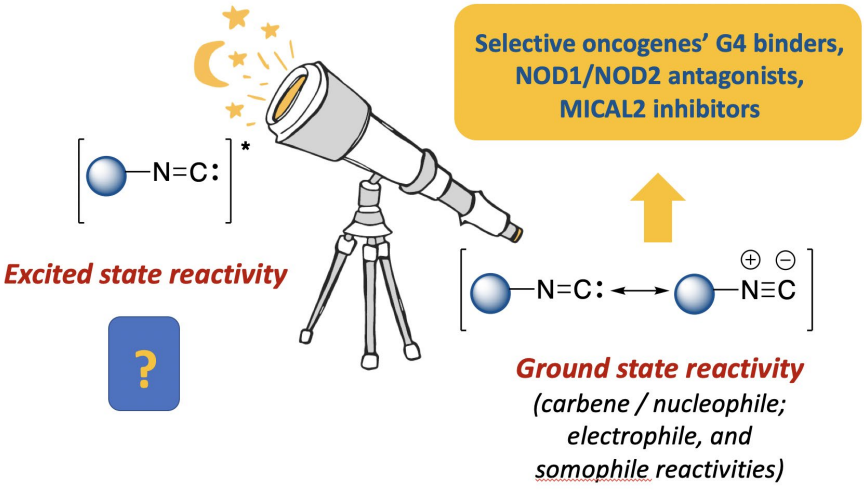
Isocyanide Chemistry from the Ground (state) to the Star(s): *what's the point for a medicinal chemist?*

Mariateresa Giustiniano

Department of Pharmacy, University of Naples Federico II, via D. Montesano 49, 80131, Napoli, Italy

Isocyanides, thanks to their multiple reactivity modes spanning from carbene/nucleophile, to electrophile, to somophile behaviours are considered a class of very special compounds.[1] The harnessing of isocyanides' ground state reactivities in medicinal chemistry programs aiming at the development of selective oncogenes' G-Quadruplex binders[2], NOD-1/NOD-2 antagonists, and MICAL-2 inhibitors will be herein presented. Furthermore, recent results about the involvement of isocyanides in photoredox catalysed processes will show how such an innovative approach could lead to the identification of green synthetic methodologies to get key structural elements such as amides[3] and *unconventional* heterocycles[4]. Finally, a focus on isocyanides' photoexcitation chemistry will reveal promising and unexpected opportunities to expand the chemical landscape of a (synthetic) medicinal chemist.



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Prospective repurposing of novel factor Xa inhibitors as blockers of TMPRSS2-mediated SARS-CoV-2 cell entry

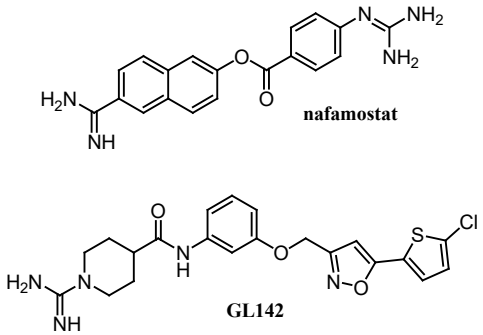
Modesto de Candia,[a] Flavio De Maio,[b] Mariagrazia Rullo,[a] Erica De Candia,[c] Gabriella Elia,[d] Maurizio Sanguinetti,[b] and Cosimo D. Altomare[a]

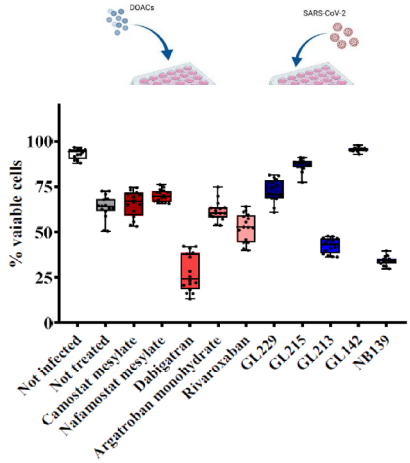
[a]Department of Pharmacy–Pharmaceutical Sciences, University of Bari Aldo Moro, Bari, Italy. [b]Dipartimento di Scienze di Laboratorio e Infettivologiche, Fondazione Policlinico Universitario A. Gemelli IRCCS, Rome, Italy. [c]Department of Translational Medicine and Surgery, Catholic University of Rome, Rome, Italy. [d]Department of Veterinary Medicine University of Bari Aldo Moro, Bari, Italy.

Besides the development of vaccines, many efforts are ongoing worldwide for discovering new druggable targets and drugs to fight Severe Acute Respiratory Syndrome Coronavirus 2 (SARS-CoV-2), triggering the pandemic Coronavirus disease 19 (COVID-19). The interstitial pneumonia caused by SARS-CoV-2 results in high mortality due to high-rate incidence of fatal disseminated intravascular coagulation (DIC), venous and pulmonary thromboembolism. In this context, observational studies have recently suggested that direct oral anticoagulants (DOACs) may protect patients with COVID-19 showing atrial fibrillation [1].

SARS-CoV-2 internalization into the host cells on the surface of lung epithelia is mediated by the interaction of the viral spike (S) glycoprotein with angiotensin converting enzyme II (ACE2) and cleavage of the S protein by the transmembrane protease serine 2 (TMPRSS2) [2]. The blood coagulation factor Xa (fXa) and thrombin (thr), expressed in pulmonary tissues, may also catalyze the S protein cleavage, which suggests fXa and thr as potential targets in antiviral drug discovery [3]. Among others, nafamostat, that is a guanidine/amidine antithrombin and antiplasmin agent, has been recently identified as covalent TMPRSS2 inhibitor [4].

Herein, we report on the effects on SARS-CoV-2-infected african green monkey kidney (VERO) epithelial cells of some isonipecotamide-based fXa/thr reversible inhibitors, synthesized [5] and tested for cytotoxicity by XTT assay. Their antiviral activity was preliminarily assessed in monolayers of VERO cells incubated with the test compounds at 100 μM concentration 2 hours before infection with SARS-CoV-2, using not treated and not infected cells as controls. After 72 hours from infection, cells were fixed and stained by using crystal violet. Within the examined series, GL142, which on the other hand displayed in silico optimal docking scoring toward fXa and TMPRSS2, proved to be promising as it showed at non-cytotoxic dose protective effects against SARS-CoV-2 even slightly stronger than nafamostat.





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From Small Molecules To PROTAC Technology: A Novel Approach To SOCE Related Diseases

Irene Preet Bhela

[a]*Department of Pharmaceutical Sciences, Università degli Studi del Piemonte Orientale, Via Bovio 6, 28100, Novara*

Store-Operated Calcium Entry (SOCE) is a complex machinery relying on two proteins (STIM and Orai) and contributing to the regulation of calcium homeostasis. Since it is involved in a wide range of cellular functions, its impairment has been associated to several diseases.[1] Among them, our group has focused on acute pancreatitis (AP)[2] and tubular aggregate myopathy (TAM)[3], two diseases that lack an effective medical treatment.

In this context, we have discovered a class of SOCE modulators, known as *pyrtriazoles*,[4] where the arylamide, shared by all the SOCE modulators reported in the literature so far, is replaced with a 1,4-disubstituted 1,2,3-triazole ring. Compound **1** (Figure 1) showed a high potency (IC_{50} = 440 nM) and demonstrated its efficacy in a mouse model cerulein-induced of AP. Nevertheless, its short half-life (i.p., 1.3 h) prevented its application in a chronic disease like TAM.

To further increase the drug-likeness of our compounds, we moved to a class of *biphenyl triazoles*.[5] Among the 41 compounds synthesized, **2** was selected for *in vivo* studies due to its promising features in terms of potency, PK parameters and aqueous solubility, and is currently being assessed *in vivo* in a model of TAM.

Despite the promising profile of our molecules, the mechanism of action still remains unclear. With the double aim of better elucidating it and of investigating a new therapeutic approach in SOCE-related diseases, in my PhD I am exploiting the proteolysis targeting chimeras (PROTACs) technology. PROTACs, which promote target protein degradation via ubiquitin-proteasome system, are heterobifunctional small molecules consisting of three chemical elements: a ligand for the protein of interest (POI), a E3 ubiquitin ligase (E3) recruiting ligand and a linker.[6] Within this project, I have synthesized a small library of PROTACs based on the structure of **2** that are currently being biologically evaluated. The challenge of this project is represented by the fact that no crystallographic information is available for human Orai and STIM and that neither of the two are cytosolic proteins.

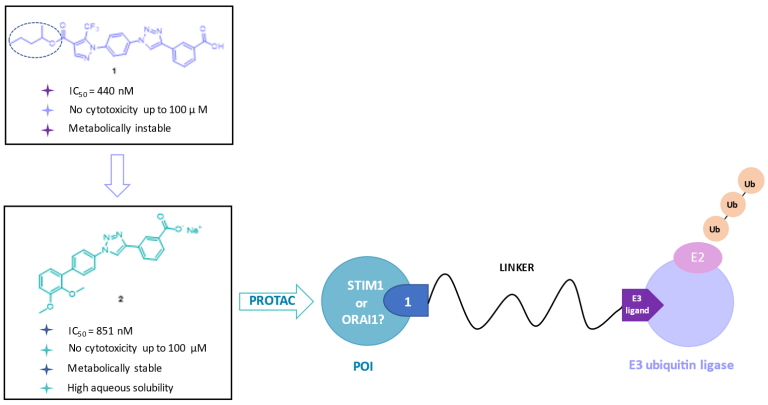

Figure 1

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Investigating the AM-001 binding site to EPAC1 protein using co-solvent molecular dynamics

Bufano M.,[a] Lezoualc'h F.,[b,c] Silvestri R.,[a] and Coluccia A.[a]

[a] *Department of Chemistry and Technologies of Drug, Sapienza University of Rome, Laboratory affiliated to Istituto Pasteur Italia – Fondazione Cenci Bolognetti, Piazzale Aldo Moro 5, I-00185 Roma, Italy*
[b] *INSERM UMR-1048, Institut des Maladies Métaboliques et Cardiovasculaires, 31432 Toulouse, Cedex 04, France*
[c] *Université de Toulouse - Paul Sabatier, 31432 Toulouse, Cedex 04, France*

The exchange proteins activated by cAMP (EPAC) are implicated in a large variety of physiological processes and they are as considered promising targets for a wide range of therapeutic applications.[1] In particular EPAC1 is considered as a novel protein target for the treatment of various cardiac diseases.[2,3] In that context, we recently characterized a selective EPAC1 antagonist named AM-001.[2] This compound was featured by a non-competitive mechanism of action but the localization of its allosteric site to EPAC1 structure has yet to be investigated. Therefore, we performed cosolvent molecular dynamics with the aim to identify a suitable allosteric binding site. The CMD led to the identification of a series of suitable pockets then studied by docking and classical molecular dynamics. This approach led us to the identification of a suitable allosteric binding pocket for AM-001. As a model validation, we also evaluated the binding poses of the available AM-001 analogues, with a different biological activity. Finally, the complex EPAC1 with AM-001 bound at the putative allosteric site was further refined by molecular dynamics. The principal component analysis led us to identify the protein motion that resulted in an inactive like conformation upon the allosteric inhibitor binding (Figure 1).

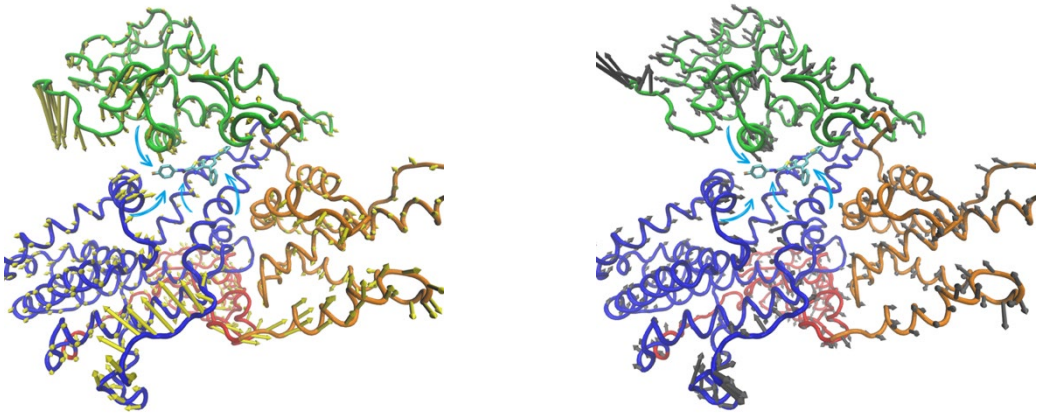

Figure 1. Porcupine plot of the top two eigenvectors. Right panel: eigenvector 1, left panel: eigenvector 2. Epac1 is reported as tube: CNBD and DEP green; REM orange; CDC25-HD blue and RA red. AM-001 is reported as cyan stick. The yellow and grey arrows attached to each a-carbon atom indicate the direction of the movement; the size of each arrow shows the magnitude of the corresponding movement.

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Towards the rationalization of agonists' activity and selectivity for melatonin receptors hMT1 and hMT2 in IOP control for glaucoma

Mattia Cantarini [a], Roberta Galeazzi [a], Dario Rusciano [b], Giovanna Mobbili [a], Cristina Minnelli [a], Emiliano Laudadio [c], Giorgia Giorgini [a]

[a]*DISVA, Università Politecnica delle Marche, via Brecce Bianche, 60131 Ancona, Italy*
[b]*Sooft Italia S.p.A. Contrada Molino, 17, 63833 Montegiorgio (FM) – Italy*
[c]*SIMAU, Università Politecnica delle Marche, via Brecce Bianche, 60131 Ancona, Italy*

An increased intraocular pressure (IOP) characterizes the majority of glaucoma forms, ocular neuropathies caused from a progressive degeneration of retinal ganglion cells. Daily IOP fluctuations are physiologically regulated thanks to antioxidant and signalling activities of melatonin, a night-time neurohormone produced from pineal gland and retinal cells[1,2]. Unlucky, melatonin has a limited employement in the treatment of altered IOP disorders for its low stability and bioavailability linked to its high antioxidant activity. Through computational methods, we aim to search compounds as potential melatonin agonists gaining more stability and bioavailability than melatonin itself. Basing on the usage of agomelatine, a melatonin-derivative with atypical antidepressant activity, we identified as targets that could be involved in IOP signalling regulation, the melatonin receptors 1 (*h*MT1) and 2 (*h*MT2) and the serotonin receptor 5HT2c[3]. We obtained promising results from High Throughput Virtual Screening (HTVS) through *Autodock Vina*[4] of ZINC15[5],using *in house* and drug repurposing compounds libraries, focusing on the orthosteric site of the identified 3D macromolecular targets' structures. Affinity values in terms of free binding energy (ΔG_{bind}) and poses of the selected compounds within the receptors pocket were optimized through dynamic molecular docking, a combination of molecular docking with AutoDock4.0[6] and atomistic molecular dynamics simulations with GROMACS 2020.2[7]. *In vitro* and *in vivo* test were performed on the most promising compounds that showed the highest affinities (low ΔG_{bind}) and poses close to the natural ligand in receptor orthosteric sites.

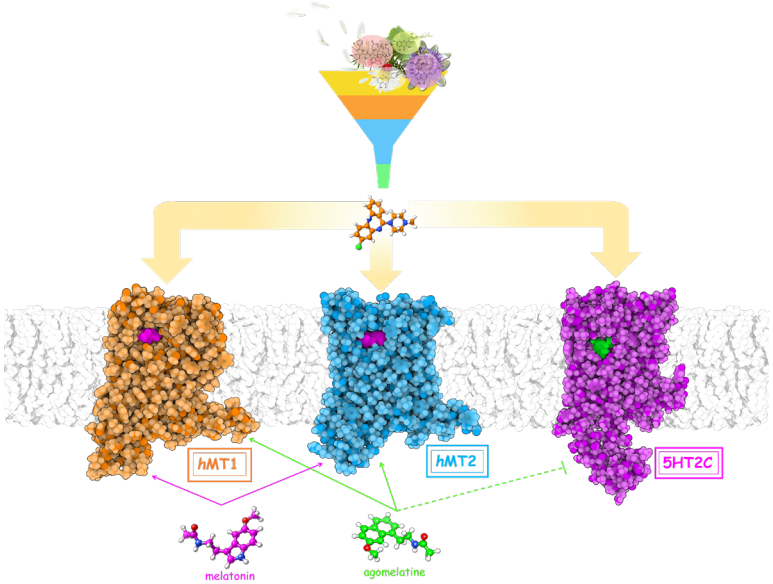

Figure 1. Set of targets binding melatonin and agomelatine have been depicted. For each HTVS-derived compounds, affinity in terms of ΔG_{bind} and its pose within receptors orthostheric site were evaluated through dynamic molecular docking.

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New imatinib-based analogues of benznidazole as anti-*Trypanosoma cruzi* agents for the treatment of Chagas disease

Valeria Ciaffaglione[a], *Sebastiano Intagliata*[a], *Luca S. F. N. de Freitas*[b], *Maria de Nazaré Correia Soeiro*[b], *Loredana Salerno*[a]

[a] *Dipartimento di Scienze del Farmaco e della Salute, Università degli Studi di Catania, Viale A. Doria 6, 95125, Catania (Italy)*
[b] *Laboratório de Biologia Celular do Instituto Oswaldo Cruz, Fundação Oswaldo Cruz, Av. Brasil 4365, Manguinhos, 21040-360 Rio de Janeiro, Rio de Janeiro, Brazil*

Chagas disease (CD) belongs to neglected tropical infections and is caused by *Trypanosoma cruzi*. The current therapy is restricted to benznidazole (BZ) and nifurtimox (NFX), which show severe side effects, low efficacy against the chronic phase, poor patient compliance, and drug resistance [1]. Therefore, there is an urgent need for an efficient treatment against both the acute and chronic phases of the disease, which causes severe burdens especially among the poorest people of tropical countries. Drug repurposing is a valuable approach for identifying new use of clinically approved molecules to treat neglected diseases, including CD. Imatinib (IM), a FDA-approved anticancer agent used for the treatment of chronic myeloid leukemia (CML), has been studied as a repurposable compound against CD. In particular, IM showed moderate *in vitro* trypanocidal activity, with an EC_{50} value of 33.6 μM against bloodstream trypomastigotes and 43.4 μM against culture-derived trypomastigotes. Moreover, an additive effect was obtained by testing IM in combination with BZ [2]. On this basis, a series of previously synthesized oxybutylimidazole derivatives, containing an IM-like portion [3], was evaluated for the potential trypanocidal activity (unpublished data). Interestingly, most of these compounds were at least twice as potent as BZ and tenfold more potent than IM against bloodstream trypomastigotes (Y strain). Based on these promising findings, in this work, we developed two new series of IM analogues (Fig. 1). The first series (**1a**–**h**) was obtained by replacing imidazole of the previous compounds with 2-nitroimidazole. The latter is present in the structure of BZ and it seems to be involved in the mechanism of action of BZ, thanks to its ability to generate free radicals that kill the parasite. The second series (**1i**–**n**) was developed by directly coupling the IM-like portion with BZ and by varying, from 1 to 3 units, the length of the spacer bound to 2-nitroimidazole or imidazole. Ongoing studies are evaluating the efficacy of these compounds against the different forms and strains of *Trypanosoma cruzi.*

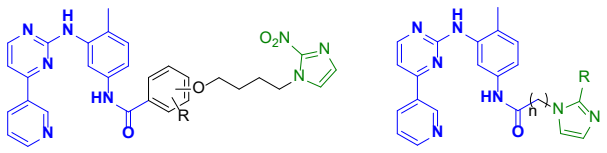

Figure 1. Chemical structure of novel IM-based derivatives. The IM-like portion is depicted in blue, 2-nitroimidazole or imidazole in green.

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Synthesis of hybrid small molecules as potential PA-PB1 heterodimer disruptors of Influenza virus Polymerase

A. Cianciusi[a]; F. Musumeci[a]; A. Carbone[a]; I. D'Agostino[b]; S. Schenone[a].

[a] University of Genoa, Department of Pharmacy, Viale Benedetto XV,3, I 16132, Italy; [b]University of Siena, Department of Biotechnology, Chemistry and Pharmacy, St. Aldo Moro 2, I 53100, Italy.

Viral RNA-dependent RNA polymerase (RdRp) is the largest functional molecular machine in Influenza (Flu) viruses, due to its pivotal role in the viral replication and transcription.
RdRp is a complex constituted by three virus-encoded subunits named PA, PB1, and PB2, bound each other non-covalently with a set of interactions that are essential for the enzymatic activity [1].
Furthermore, since the Flu RdRp is significantly different from human polymerases and is highly conserved among the different Flu strains, compounds targeting this protein complex could be less prone to induce drug-resistance [2]. Thus, Flu polymerase is considered a promising and druggable target and several anti-Influenza agents, acting through a protein–protein interaction (PPI) inhibition strategy, have been developed in the last decade [3].
In particular, among the interactions of the heterotrimeric complex, the one between the PA-PB1 subunits has stood out as the most interesting because occurs among relatively few amino acid residues, indicating the feasibility of small-molecule drug design [4]. In this context, my research group has identified, through a high-throughput docking study, a family of molecules possessing a 3-cyano-4,6-diphenylpyridine scaffold, that has been optimized in order to get more potent PA-PB1 heterodimer inhibitors.
As a result, a first generation of amino acid derivatives (**1**, Figure 1) has been successfully synthesized and tested [5]. In addition, a second generation of more active compounds with a pyrimidine or pyridine nucleus (**2**, Figure 1) but lacking the cyano moiety has been developed.
Based on the interesting obtained results, we decided to carry out a Mix&Match approach to expand structure-activity relationship (SAR) evaluation and obtain a new library of potentially more active PA-PB1 disruptors (**3**, Figure 1).
Biological evaluation on the third new generation of derivatives are currently in progress.

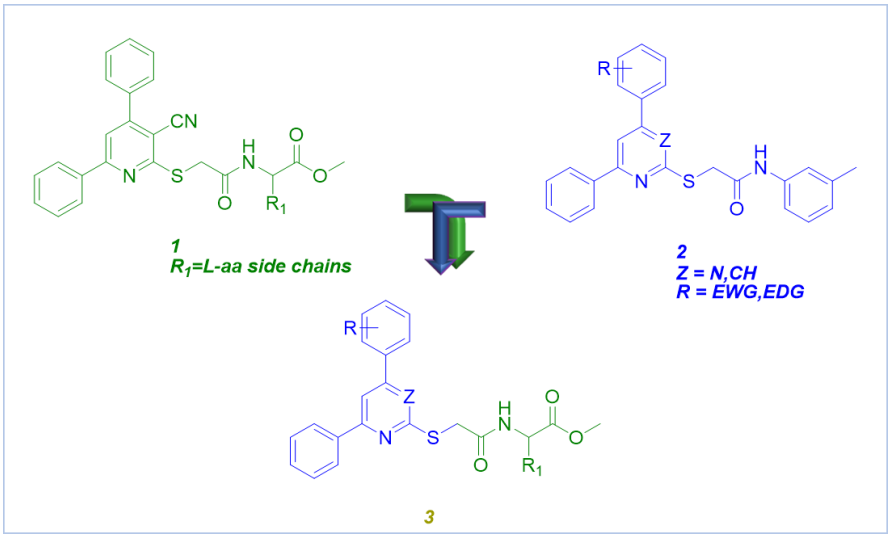

Figure 1: **Schematic representation of the Mix&Match approach**

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Quinolonyl derivatives endowed with a unique mechanism of action against HIV-1 integrase

De Leo, A.;[a] Ialongo, D.;[a] Messore, A.;[a] Scipione, L.;[a] Kvaratskhelia M.;[b] Di Santo, R.;[a] Costi, R.[a]

[a]Istituto Pasteur-Fondazione Cenci Bolognetti, Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza University of Rome, P. le Aldo Moro 5, 00185 Rome, Italy
[b]Division of Infectious Diseases, University of Colorado School of Medicine, Aurora, United States

Over the past three decades, the outcome of HIV infection has been revolutionized by considerable progress in the therapeutic options available, as a result of the introduction of effective multi-pills regimens (HAART). Although HAART is purposely devised to overcome the high viral genetic variability and the subsequent emergence of resistance, multi-drug resistant strains can still be detected in some patients and long-term drug toxicities still represent an unresolved concern in HIV management [1].
HIV integrase (IN) is vital for viral replication and it is an important therapeutic target. In this regard, integrase strand transfer inhibitors (INSTIs) which bind to the active site of the viral enzyme, have proven to be highly effective, becoming a potent first-line therapy to treat infected patients.
On the other hand, allosteric inhibitors of integrase (termed ALLINIs) are a promising new class of antiretroviral agents, which are not yet a clinically approved therapeutic option, but represent a relevant scientific area of interest for anti-HIV research. These inhibitors act differently in respect to INSTIs, in fact, they interfere with viral maturation in the late steps of the infection, exhibiting only modest activity in the early steps. They induce a higher order multimerization of IN and they impair the correct IN-vRNA interaction which is fundamental for the generation of fully competent virions. As a result, defective viral particles with greatly reduced infective potential are produced and mis-localization of the vRNA outside the viral capsid is generally observed [2].
We therefore decided to explore and characterize the mechanism of action of a small subset of quinolyl based compounds belonging to our in-house library, previously screened against IN. We assessed the capability of our derivatives to inhibit at low micromolar concentrations both the IN 3'-processing (3'-P) and strand transfer (ST) reactions in a LEDGF/p75 independent assay. In addition, we performed *in vitro* binding assays, and we found that our quinolonyl derivatives are able to disrupt the IN-vRNA interaction, that is vital for a correct generation of a functional infective virion.
In conclusion, we identified quinolonyl derivatives endowed with a unique mechanism of action based on i) the interference on both 3'-P and ST steps of the IN activity, and ii) the ability to hamper the IN-vRNA interaction during the late steps of HIV life cycle. The discovery of this unique mechanism of action can pave the way for the development of a new inhibition strategy against IN.

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Design, synthesis, and anticancer activity of novel dual HDAC1,2/LSD1 inhibitors

Elisabetta Di Bello[a], *Sergio Valente*[a], *Antonello Mai*[a]

[a] *Department of Drug Chemistry and Technologies, Sapienza University of Rome, P. le A. Moro 5 00185 Rome (Italy)*

Cancer is a multifactorial disorder caused by genetic and/or epigenetic alterations leading to the misregulation of numerous pathways. The simultaneous inhibition of two or more targets involved in cancer pathogenesis, by drug combination or by a single 'hybrid molecule,' can improve therapeutic efficacy over a single-target inhibitor (*1*). Hybrid drugs can benefit from a more predictable and less complex metabolism, more favourable pharmacokinetic and pharmacodynamic parameters, and improved bioavailability besides improved patient compliance and reduced costs (*2*).In the last two decades, histone deacetylase inhibitors (HDACi) emerged as very effective tools in cancer research and pharmacology. They activate or modulate multiple antitumor pathways, such as apoptosis, expression of nonhistone proteins, transcription factors, inflammation/immune response mediators resulting in growth arrest, cell death, senescence, and anti-angiogenic effects (*1*). More recently, it is finding that LSD1 plays a pivotal role in promoting cell proliferation and development; moreover, seems also to stimulate cell migration, invasion, and metastasis by inducing the epithelial-mesenchymal transition (EMT) (*3*). The simultaneous blockage of HDAC1/2 and LSD1 has been considered a promising strategy against cancer, leading to combination studies and hybrid compound development. Recently, combining the pharmacophoric elements of the LSD1i TCP with the zinc-binding group of entinostat, we first identified the compound corin, targeting the ternary CoREST complex and inhibiting both LSD1 and HDAC1 at submicromolar doses (*4*). In a panel of melanoma cells, corin treatment resulted in higher proliferation inhibition than the single agents; cell studies confirmed the dual-inhibition mechanism of corin(*4*). Prompted by the strong anticancer effects of corin, we plan to develop new GSK2879552- and ORY-1001-based hybrids (**Figure 1**), which could specifically inhibit HDAC1 and/or HDAC2, partners of LSD1 and CoREST in repressor complexes. **Figure 2** shown the first two hybrids inhibitor MC4358 and MC4359. MC4359 displayed nanomolar inhibition against HDAC1, being 365-fold selective over HDAC3, dual-digit micromolar inhibition against HDAC6 and HDAC8, not active against HDAC4, and submicromolar inhibition against LSD1. Following, in several solid cancer cell lines, such as lung A549, colon HCT-116, and breast MCF7 cancer cell lines, MC4359 displayed a remarkable blockage (over 80% in MCF7 at 5 μM and 24 h) of the cell cycle in the pre-G1 phase, thus preliminarily indicating apoptosis induction. The same compound was clearly able to time-dependently increase histone 3 acetylation (AcH3) and histone 3 lysine 4 (H3K4Me2) methylation, thus proving the simultaneous engagement of both HDAC and LSD1 targets in MCF7 cells.

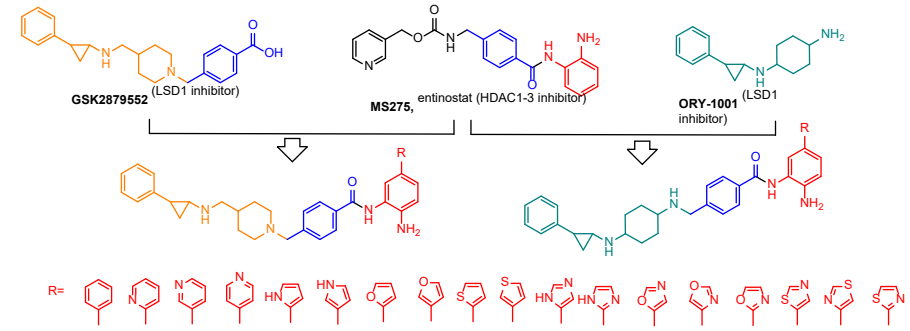

Figure 1. Design of novel dual HDAC1,2/LSD1 hybrid inhibitors

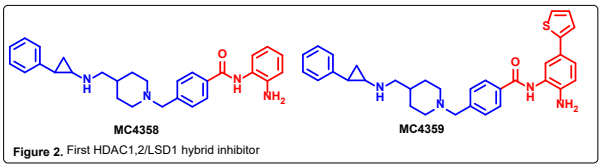

Figure 2. First HDAC1,2/LSD1 hybrid inhibitor

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Synthesis and biological evaluation of new pyrazole carbohydrazides as antiproliferative and antioxidant agents

M. Lusardi [a], C. Brullo [a], M. G. Signorello [a], M. Ponassi [b], E. Iervasi [b], A. Spallarossa [a]

[a] *Department of Pharmacy, University of Genova, Genova, viale Benedetto XV, 3, 16132 Genova, Italy*
[b] *IRCCS Ospedale Policlinico San Martino, Proteomics and Mass Spectrometry Unit, L.go R. Benzi 10, 16132 Genova, Italy*

5-Amino pyrazole carbohydrazides **1** (Figure 1) showed promising antioxidant activity, inhibiting reactive oxygen species (ROS) elevation in neutrophils. In previous structure-activity relationship (SAR) studies the free ammino group proved to be an important structural determinant for activity [1-3].

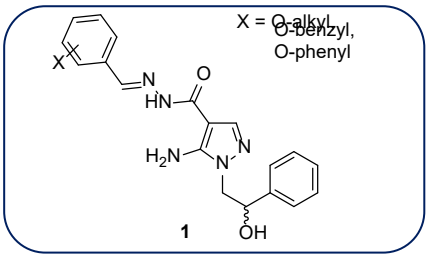
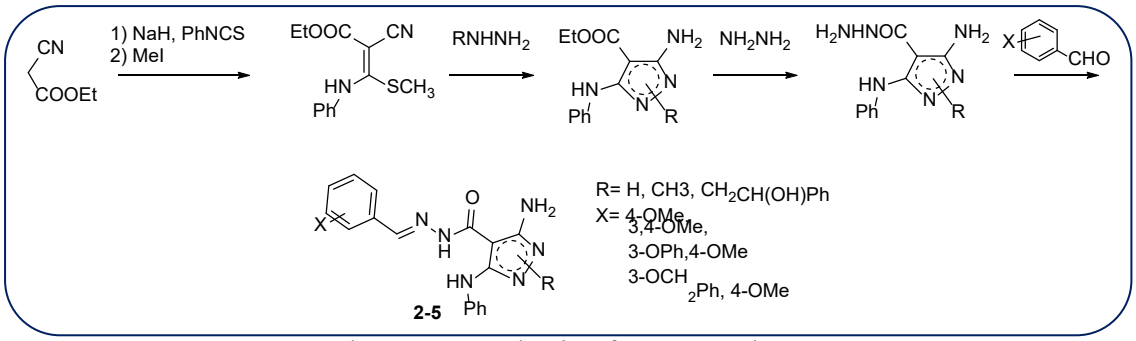


Figure 1. Chemical structure of compounds **1**

In order to further extend the SARs of this class of compounds, the synthesis of benzylidene pyrazole carbohydrazides **2-5** was carried out (Scheme 1). The new derivatives share with the parent compounds the free amino group but bear an additional N-phenyl substituent on the pyrazole scaffold. Furthermore, different regioisomers were prepared to evaluate the effect of the pyrazole N-substitution on activity.



Scheme 1. Synthesis of compounds **2-5**

The antiproliferative activity of compounds **2-5** was preliminarily tested in cell-based assay on a large panel of cancer cell lines. Additionally, the ability of the prepared derivatives to inhibit ROS formation and aggregation was tested on human platelets. The synthetic procedure, the structural assignments as well as the biological properties of the prepared compounds will be presented and discussed in the poster.

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Carnosine Derivatives: The Role of Secondary Amines in The Quenching Mechanism of Reactive Carbonyl Species

Sarah Mazzotta, Ines Sanz, Giancarlo Aldini, Giulio Vistoli, Luca Regazzoni, Laura Fumagalli

Dipartimento di Scienze Farmaceutiche, Università degli Studi di Milano, Via L. Mangiagalli 25, 20133 Milano, Italy.

Reactive carbonyl species (RCS) are electrophilic compounds generated by sugar oxidation and lipid peroxidation of ω-6 polyunsaturated fatty acids (PUFAs). The most abundant RCS are the α,β-unsaturated aldehydes 4-hydroxy-trans-2-nonenal (HNE) and acrolein (ACR), but also the dialdehydes glyoxal (GO) and malondialdehyde (MDA), that can react with nucleophilic functions of nucleic acids and proteins, such as histidine, cysteine, or lysine residues, forming stable Michael adducts [1]. High levels of RCS cause carbonyl stress, that contributes to aging, atherosclerosis, diabetes, renal failure, glucose intolerance and hyperglycemia, and neurodegenerative diseases. For these reasons, RCS get attention in the field of medicinal chemistry as drug targets for nucleophilic compounds that have a scavenging group, such as thiol, imidazole, or primary amine [2]. L-carnosine is an endogenous dipeptide constituted by L-histidine and β-alanine (Figure 1), that is able to quench α,β-unsaturated aldehydes, such as ACR and HNE by providing unreactive adducts. The quenching activity is associated to the nucleophilicity of both β-alanine amino group, that generate a stable Schiff base with the aldehyde, and the Nτ of the histidine group, that furnish a Michael adduct with the C3 of the unsaturated aldehydic group. Unfortunately, the therapeutic use of L-carnosine is limited because of its instability in human plasma, due to the rapid hydrolysis by the carnosinase dipeptidase [3].

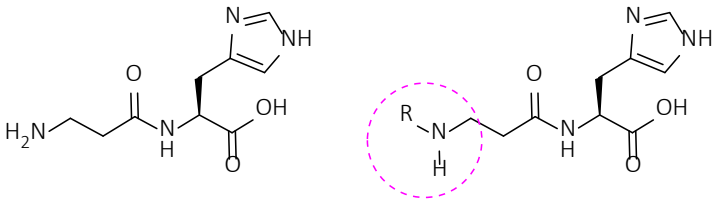

Figure 1. General structure of new carnosine derivatives as potential scavengers of RCS.

The aim of the present study was to investigate the role of secondary amines in quenching activity of reactive carbonyl species, by generating a new small set of carnosine derivatives (Figure 1). Our design is headed toward the introduction of different substituents on β-alanine amino group, in order to examine the impact of the size, steric hindrance and electronic properties on the reactivity as potential scavengers. For the preparation of new compounds several synthetic routs have been performed, followed by their structural characterization through NMR spectroscopy.
All synthesized compounds have been assayed for their quenching reactivity against HNE, monitoring the kinetic by HPLC-UV analysis, and the formation of corresponding adducts through mass spectrometry analyses. Furthermore, the metabolic stability study of the tested compounds in human serum has been also performed.

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New Pyrazolo[1,2-a]benzo[1,2,4]triazine-3-one derivatives as potential SARS-CoV-2 protease modulators

[a]Francesco Mingoia, [b]Maria Concetta Vitale, [b]Gabriele La Monica, [b]Alessia Bono, [b]Antonino Lauria, [b]Annamaria Martorana

[a] [1]Istituto per lo Studio dei Materiali Nanostrutturati (ISMN- CNR), Via U. La Malfa 153, 90146 Palermo, Italy; [b]Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche (STEBICEF), Sezione di Chimica Farmaceutica e Biologica, Università di Palermo, Viale delle scienze, Palermo.
francesco.mingoia@ismn.cnr.it

Due to the widespread pandemic COVID-19 emergency, the scientific community is frenetically working on the identification of targeted therapeutic strategies against the new pathogen SARS-CoV-2. In addition to the primary role played by the development of efficient vaccines, the discovery of small molecules, capable to interfere with the infection and reducing the related symptoms, may help in the etiological eradication of the virus.
Up to date, several computational and in wet studies lighted the mechanism of infection and the viral protein pattern involved in the replication processes of the SARS-CoV-2, providing important data for the design of new molecules with a selective effect on the viral infection [1,2].
For this aim, the SARS-CoV-2 Main Protease (M^{pro}), with the crucial role to cleave the coronavirus replicase polyprotein, has been identified as a key antiviral target.
In this light, we focused our studies on the design, synthesis, and biological evaluation of a new series of pyrazolo[1,2-a]benzo[1,2,4]triazine-3-one derivatives (Figure 1), with an inhibition effect on the M^{pro} of the SARS-CoV-2.
Mixed ligand and structure-based protocols were applied for the evaluation of a large *in house* database of structures. The analysis of the *in silico* data allowed identifying the set of pyrazole-benzotriazine derivatives as interesting modulators of the M^{pro}. Further computational studies were performed on a focused library, examining the pyrazole-benzotriazines scaffold with extended combinations of substituents (R^1-R^9).
The pyrazole-benzotriazine compounds, with the best *in silico* scores, were successfully synthesized following appropriate synthetic pathways. Currently, the binding assays of the new small molecules with the SARS-CoV-2 Main Protease are ongoing.

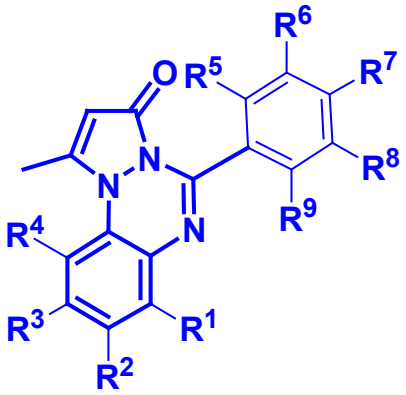

Fig.1

[1] Jin et al. *Nature* **2020**, *582*, 289.
[2] Zhang et al. Science. 2020 368, 409-412.

Low-Molecular-Weight Phosphatase B (LMW-MPtpB) inhibition as a strategy to identify new drug candidates against tuberculosis

Matteo Mori [a], Giulia Cazzaniga [a], Laurent R. Chiarelli [b], Giovanni Stelitano [b], Samuele Ciceri [a], Tiziano Tuccinardi [c], Giulio Poli [c], Fiorella Meneghetti [a] and Stefania Villa [a]

[a] Dipartimento di Scienze Farmaceutiche, Università degli Studi di Milano, via L. Mangiagalli 25, 20133 Milano, Italy; [b] Dipartimento di Biologia e Biotecnologie "Lazzaro Spallanzani", Università degli Studi di Pavia, via A. Ferrata 9, 27100 Pavia, Italy; [c] Dipartimento di Farmacia, Università di Pisa, via Bonanno Pisano 6, 56126 Pisa, Italy.

The last WHO Global TB Report estimated that 10 million people worldwide fell ill with tuberculosis (TB) in 2019 [1]. The resistance to anti-TB drugs is a global health problem that interferes with the progress of TB eradication. Hence, novel and more effective anti-TB drugs acting on unexplored targets are needed to contrast the resistance phenomenon and the progressive loss of antibiotic efficacy, and to improve the current therapies. *Mycobacterium tuberculosis* (Mtb) secretes two Low-Molecular-Weight Phosphatases (LMW-PTPs) [2], MPtpA and MPtpB, inside the cytoplasm of host macrophages. These enzymes are indispensable for the intracellular survival of Mtb because they interfere with the host immune response, thus allowing bacteria to evade the immune system. For this reason, MPtpA and MPtpB were validated as promising targets for the development of innovative antitubercular agents.

Recent computational studies defined a new pharmacophore model, which was applied to screen two commercial databases, Vitas-M and Enamine. These virtual screening experiments led to the selection of 8 molecules for MPtpB inhibition (see Figure 1).

The biological data will be discussed, along with preliminary investigations on the most promising candidates.

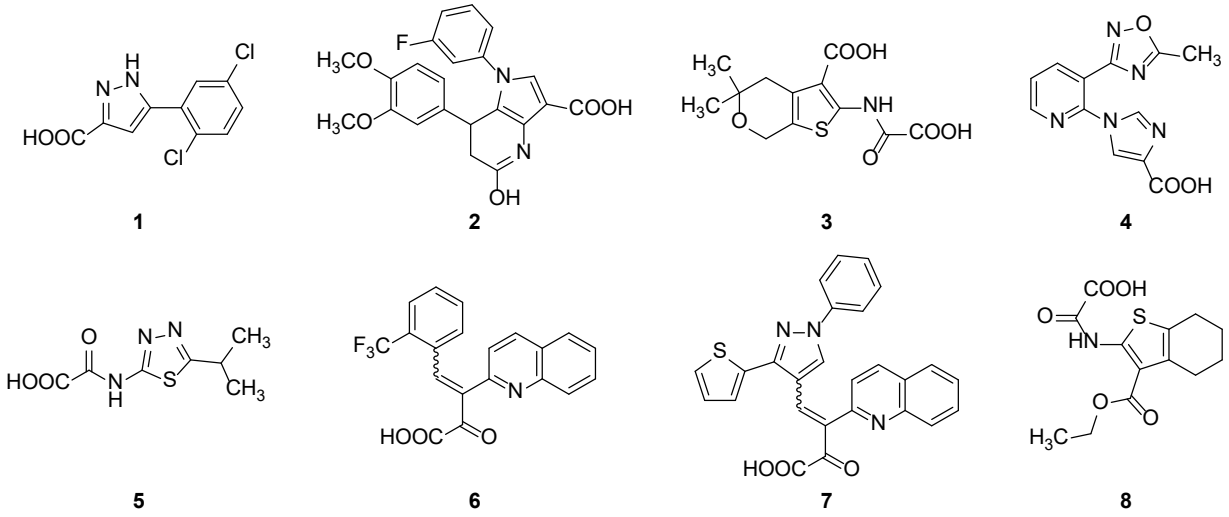

Figure 1. Molecules selected using the virtual screening approach on MPtpB.

[1] Global tuberculosis report 2020. Geneva: World Health Organization; 2020. Licence: CC BY-NC-SA 3.0 IGO

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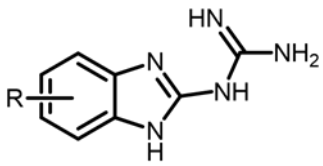
Development of guanidino-containing benzimidazoles as novel folate enzymes inhibitors for the treatment of Human African Trypanosomiasis

Marco Rizzo,[a] *Valeria Francesconi,*[a] *Elena Cichero,*[a] *Silvia Schenone,*[a] *Lorenzo Tagliazucchi,*[b] *Anabela Cordeiro-da-Silva,*[c] *Maria Paola Costi,*[b] *Michele Tonelli*[a]

[a] *Department of Pharmacy, University of Genoa, viale Benedetto XV 3, 16132, Genoa, Italy;* [b] *Department of Life Science, University of Modena and Reggio Emilia, via Campi 103, 41125 Modena, Italy;* [c] *Instituto de Investigação e Inovação em Saúde and IBMC-Institute for Molecular and Cell Biology, Universidade do Porto and Departamento de Ciências Biológicas, Faculdade de Farmácia da Universidade do Porto (FFUP), 4150-180 Porto, Portugal.*

Human African trypanosomiasis (HAT, also known as sleeping sickness) is a vector-borne parasitic infection caused by *Trypanosoma brucei* (*Tb*) parasite. Current drugs against this endemic disease are suboptimal, showing several limitations in terms of safety, efficacy and route of administration. Moreover, the emergence of drug resistant parasites jeopardizes the positive therapy outcome. These conditions claim the need of addressing more adequate therapies. In this context, pursuing our investigation on anti-protozoan agents [1-4] we considered interesting to synthesize a set of 2-guanidinobenzimidazoles (**A**) and their related 2-aminotriazino[1,2-a]benzimidazole derivatives (**B**), obtained by a ring annellation reaction. The conceived library underwent *in vitro* evaluation against *T. brucei* parasites, proving to be effective in the low micromolar range. On the base of their structural features resembling those of bi- and tricyclic folate enzymes inhibitors previously described [3, 4], we screened them against dihydrofolate reductase (*Tb*DHFR) and pteridine reductase 1 (*Tb*PTR1) enzymes of *T. brucei*, with a view to investigating their mechanism of action. Recently, the combined inhibition of PTR1 and DHFR activities in *Trypanosoma* parasites has emerged as a promising strategy for the development of more effective treatments for HAT [4]. The SAR analysis derived from this study has led to obtain key insights for the future design of more promising dual inhibitors.



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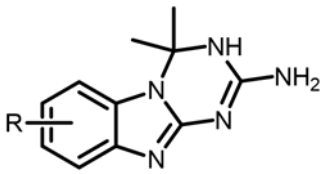

B

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Identification of small molecules against SARS CoV-2 non-structural proteins by combined multi-targeting approach and supervised machine learning

Isabella Romeo[a,b], Antonio Lupia[b], Carmine Talarico[c], Annamaria Zimbo[a] and Stefano Alcaro[a,b]

[a] Dipartimento di Scienze della Salute, Università "Magna Græcia" di Catanzaro, Campus "S. Venuta", Viale Europa, 88100 Catanzaro, Italy; [b] Net4Science Academic Spin-Off, Università "Magna Græcia" di Catanzaro, Campus "S. Venuta", Viale Europa, 88100 Catanzaro, Italy; [c] Dompé Farmaceutici SpA, Via Campo di Pile, I-67100 L'Aquila, Italy

Severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) is distinctly infective, and there is an ongoing effort to find a cure for this pandemic. Hence, speeding up drug discovery is urgently required. A combined *in silico* workflow (multi-targeting approach, virtual screening, molecular docking and supervised machine learning algorithms) to identify novel drug candidates against SARS-CoV-2 was applied in the present study. Thus, the characterization of the druggable binding pockets including both orthosteric and allosteric sites of SARS-CoV-2 non-structural proteins (nsp) were adopted for the structure-based virtual screening [1]. Many chemical libraries, consisting of commercial compounds with a molecular weight lower than 330 kDa provided by the Mediate project (https://mediate.exscalate4cov.eu), were used to select compounds interacting with SARS-CoV-2 nsp proteins (nsp7-nsp8-nsp12, nsp9, nsp10-nsp14 and nsp10-nsp16). Among around three million small molecules, nine compounds showed the best multi-targeting profile against four binding pockets of the analysed SARS-CoV-2 druggable targets. Interestingly, the indole derivatives resulted as promising *hits* by our computational protocol, emphasizing its role in designing and discovering the much-awaited anti-SARS CoV-2 therapy.[2]
The *in vitro* anti-SARS-CoV-2 activity of the candidate compounds will be investigated further for complete understanding and confirmation of their inhibitory potential.

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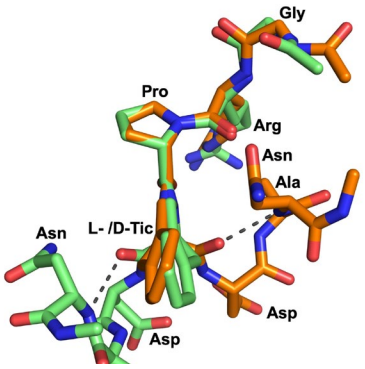
Antagonizing S1P3 receptor with cell-penetrating pepducins in skeletal muscle fibrosis

Antonia Scognamiglio[a], Angela Corvino[a], Gianluca Esposito[a], Giovanna Esposito[a], Vincenzo Santagada[a], Antonio Lavecchia[a], Alessandra Lo Bianco,[a] Fiorentina Roviezzo[a], Chiara Donati[b], Beatrice Severino[a]

[a]Department of Pharmacy, School of Medicine, University of Naples Federico II, Italy; [b]Department of Experimental and Clinical Biomedical Sciences, University of Florence, Italy

Bioactive lipids, derived from the metabolism of plasma membrane, are important mediators of cellular signaling in vertebrates. In recent years there has been a growing interest on sphingosine-1-phosphate (S1P) which is the final metabolite produced during the sequential degradation of plasma membrane glycosphingolipids and sphingomyelin. The S1P acts through five known subtypes of heptameric G-protein coupled receptors (GPCR), namely S1P1-S1P5 (S1PR). Recent evidence indicates that S1P signaling axis contributes to the development and maintenance of the fibrotic process [1]. Fibrosis is a pathological condition that can affect every organ, consequence of a persisting inflammatory and tissue remodeling condition. In different fibrotic models an extensive crosstalk between TGFβ and S1P signaling axis has been demonstrated. S1P3 plays a pivotal role in fibrosis development in different tissues such as skeletal muscle, liver, and kidney [2]. Thus, selective antagonists of the S1P3 receptor could be useful to deeply study its role in fibrosis as well as to develop new therapeutic entities to treat fibrotic diseases.

Pepducins specifically target the intracellular loops, acting as allosteric modulators of GPCR activity. Using this approach, we have synthesized a pepducin based S1P3 antagonist namely **KRX-725-II** (Myristoyl-GRPYDAN-NH_2) [3]. Here to improve the S1P1 vs S1P3 selectivity, we have synthesized several derivatives of **KRX-725-II** pointing our attention on the aromatic residue of the sequence, Tyr4, and with the aim to introduce molecular constraints. The new molecular entities have been evaluated for their selectivity profile by using mouse aortas. This screening allowed us to identify compounds **V** and **VII** (embodying respectively L- and D-Tic) as the most selective S1P3 antagonists. The selected compounds also displayed the ability to significantly reduce the profibrotic action of TGFβ1 in C2C12 myoblasts. To explain the higher selectivity observed for compounds **V** and **VII**, they were analyzed by Molecular Dynamics (MD) Simulations. The middle conformations of **V** and **VII** were compared by superimposing their GRP residues, which adopt a similar backbone orientation (see Figure). This revealed that the DAN residues with β-turn-like motif are located on opposite sides of the plane defined by the L- or D-Tic residue. This difference may explain, in structural terms, the selective S1P3 antagonism of **V** and **VII** in comparison to the unselective antagonist **KRX-725-II**, whose flexibility seems to be high enough for the adaptation to the binding regions of the individual receptor subtypes S1P1 and S1P3. Peptides **V** and **VII** possess, indeed, a highly constrained D- or L-Tic residue that hinder the pharmacophore from interacting properly with the binding pocket of the S1P1 receptor, therefore leading to S1P3 selectivity.



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Design, synthesis and biological evaluation of new anti Sars-Cov 2 agents

Smaldone G., [a] *Di Matteo F.,* [a] *Ciaglia T.,* [a] *Ostacolo C.,* [a] *Vestuto V.,* [a] *Novi S.,* [a] *Andrei G.,* [b] *Gomez-Monterrey I.,* [c] *Campiglia P.* [a]

[a] *Department of Pharmacy, University of Salerno;* [b] *Department of Microbiology, Immunology and Transplantation, Leuven;* [c]*IDiBE, Universitas Miguel Hernández of Elche*

Coronavirus disease 2019 (Covid 2019) is caused by Sars-Cov-2 (severe acute respiratory syndrome coronavirus 2), that belongs to betacoronaviridae family. [1] Sars-cov-2 genoma is a positive-sense RNA strand codifying for 27 non-structural and structural proteins of which 4 play a pivotal role in infectious cycle and for that considered as principal pharmacological targets: spike protein, RNA-dependent RNA polymerase, and two different proteases, MPro and PLpro. [2] Actually, the only antiviral drug approved for Covid treatment is Remdesivr, an ebola RDRP inhibitor, derived from a drug repurposing campaign. This approach was very useful to face the pandemic situation but cannot be the only strategy to resolve the emergency. [3,4] It is evident how the identification and the development of a new, specific anti-sars-cov-2 addressed treatment is needed. The pandemic is still in progress, causing non only the hardest sanitary crisis in the last century, but also an unrecoverable socio-economic collapse. Despite all the efforts in the last year addressed to build an efficient vaccine campaign the virus spread is still ongoing, and the challenge is still open. For these reasons the main effort of the research is to find compounds with higher selectivity and potency to fight this global pandemic. In the present paper we describe the design, synthesis and biological evaluation of a new series of compounds designed as Sars-Cov-2 Mpro inhibitors. [5] We decided to explore covalent and non-covalent inhibition using as peptidomimetic as well small molecules approach. These compounds were firstly screened by an enzymatic assay, evaluating the compound induced displacement of a fluorescent substrate of MPro from its binding site, and then against two different clinical isolates of SARS-CoV-2 in Vero cells. The most interesting result, is about compound **29**, showing an activity against both Sars-cov-2 strains comparable to Remdesivir and a negligible cytotoxicity. Interestingly, this compound is the most effective in inhibiting MPro, so its antiviral mechanism could likely be due to this process. To assess the selectivity of most potent compound, we tested **29** against Vero cells transfected with CMV and VZV. The compound didn't show a significative activity in this screening, highlighting its selectivity on Sars-Cov-2.

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Synthesis of new molecular hybrids of antiglaucoma drugs and H_2S donors

Rosa Sparaco [a], Elisa Magli [a], Valentina Citi [b], Francesco Frecentese [a], Giuseppe Caliendo [a], Elisa Perissutti [a], Vincenzo Calderone [b], Ferdinando Fiorino [a]

[a] *Department of Pharmacy, University of Naples "Federico", Via D. Montesano 49, Naples, Italy*
[b] *Department of Pharmacy, University of Pisa, Via B. Pisano 5, Pisa, Italy*

Glaucoma is a group of optic neuropathies consisting of retinal ganglion cells (RGCs) and axonal death with corresponding loss of field vision. This disease is one of the leading causes of irreversible blindness globally. Hydrogen sulfide (H_2S) is a gaseous neurotransmitter implicated in various pathophysiological processes. It is involved, in particular, in the pathological mechanism of glaucomatous neuropathy. It has been reported that retinal H_2S endogenous levels markedly decrease in glaucoma animal model. In addition, exogenous H_2S supplement effectively attenuates the apoptosis of RGCs in experimental models [1].
The aim of this project is to synthesize new drugs which combine the action of antiglaucoma drugs and H_2S released by "molecular donors", through different chemical and enzymatic mechanisms, to provide a synergistic heightened therapy.
The molecular hybrids were synthetized by coupling antiglaucoma drug with H_2S donors. The H_2S-release properties of the new compounds were evaluated by amperometric approach. The generation of H_2S was tested in a phosphate buffer solution in the presence or in the absence of L-Cysteine 4 mM. A further evaluation was performed to study the H_2S release in retinal cells by spectrofluorometric measurements using WSP-1, a fluorescent probe which specifically and irreversibly interacts with H_2S. The fluorescence produced by this interaction was quantitatively recorded by a spectrofluorometric approach and also observed by fluorescence microscopy.
Brinzolamide, betaxolol and brimonidine were coupled with different H_2S donors such as 4-hydroxybenzothioamide (TBZ), 5-(4-hydroxyphenyl)-3H-1,2-dithiole-3-thione (ADT-OH), S-ethyl 4-hydroxybenzodithioate (HBTA) and 4-hydroxyphenyl isothiocyanate (HPI).
The amperometric assay demonstrated that in the absence of L-Cys, all the compounds showed a completely negligible release of H_2S. The curves H_2S-release vs time in the absence or in the presence of L-cysteine for betaxolol hybrids were almost overlapping, showing poor H_2S generation. This effect may be due to the chemical structure of betaxolol that makes the H_2S releasing agent more susceptible to hydrolysis. Instead, the preincubation with an excess of L-Cys (4 mM) improved the H_2S release from the brinzolamide and brimonidine hybrids. Noteworthy, the compounds brinzolamide-HBTA and brimonidine-HPI showed the best H_2S releasing profiles. The maximal concentration of H_2S (C_{max}) generated from these compounds upon incubation (for 30 min) in the presence of L-Cys, was respectively 3 μM and 6 μM.
The evaluation of H_2S release on retinal cells by spectrofluorometric measurements is still ongoing.
In conclusion, novel H_2S-donor hybrids using as native drugs brinzolamide, betaxolol and brimonidine were synthetized. In the amperometric assay, among the series of synthetized molecules, brinzolamide-HBTA and brimonidine-HPI exhibited a progressive and time related slow H_2S-releasing profiles in the presence of L-Cys. Finally *in vitro* studies, currently in progress, will evaluate the ability of the new hybrids to release H_2S in retinal cells, without adding exogenous thiol.

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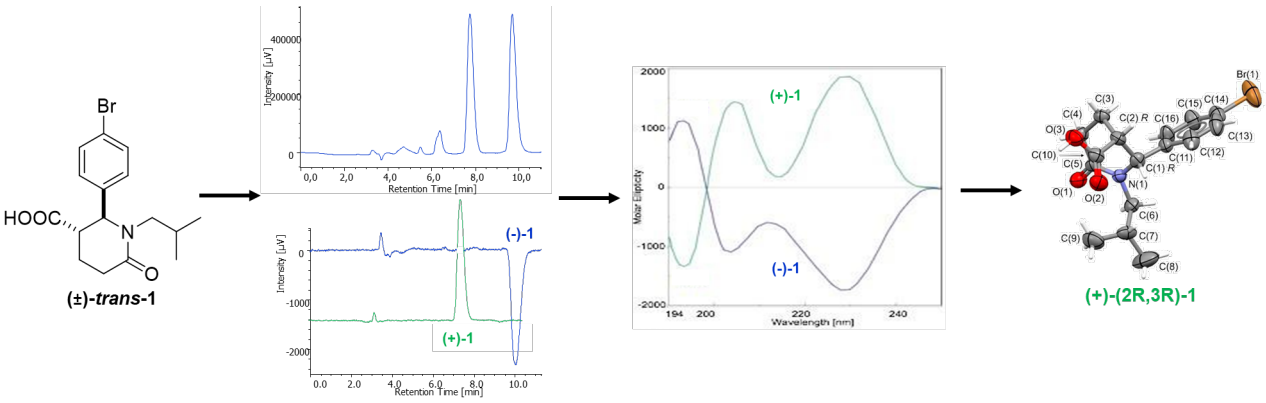
Chiral resolution and absolute configuration of substituted lactams, as key intermediates for the synthesis of pharmaceutical interest compounds.

Rita Stabile[a], Roberta Listro[a], Pasquale Linciano[a], Daniela Rossi[a],Massimo Boiocchi[b], and Simona Collina[a]

[a] Department of Drug Sciences, University of Pavia, Viale Taramelli 12, Pavia, Italy; [b] Centro Grandi Strumenti, University of Pavia, via Bassi 21, 27100 Pavia, Italy

Chiral γ and δ-lactams rings are key pharmacophores in pharmaceuticals and bioactive natural products, making libraries of these building blocks a valuable resource for drug discovery and development campaigns. Here, we report the synthesis, chiral resolution and absolute configuration (AC) assignment of the δ-lactam 2-(4-bromophenyl)-1-isobutyl-6-oxopiperidin-3-calboxylic acid **1**. The synthesis *via* Castagnoli-Cushman reaction yielded predominantly the trans-configured racemic mixture [1]. To isolate enantiomeric **1** we exploited enantioselective HPLC-UV/ECD system.

Upon screening different chiral stationary phases (CSPs) and eluent mixtures, a baseline separation of the enantiomers was obtained using Chiralpak IA column eluting with n-Hex/EtOH/DEA/TFA (90:10:0.1:0.3, v/v/v/v). The analytical conditions were properly transferred to semipreparative scale, thus furnishing the enantiomers with an *e.e.*>99%.
To assign the AC, the enantiomers were crystalized by vapor diffusion, using IPA as solvent and water as precipitant. The subsequent X-ray diffraction analysis on the (+)-**1** showed that its AC is 2R,3R. Therefore, the 2S,3S configuration was attributed to (-)-**1** [2].



Compound **1** has been used by our group as reference compound for assigning the AC to its derivatives and to structurally related lactam, exploiting an empirical approach based on the comparison of elution order and ECD profile. Examples will be herein presented.
Based on our experience, this approach may be exploited for the AC assignment to a wide range of γ and δ-lactams undergoing drug discovery campaign.

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Design, synthesis and biological activity of garcinoic acid bioisosters as Pregnane X Receptor modulators

Shiva Tali Shandiz[a], Desireé Bartolini[a], Francesca De Franco[b], Daniela Passeri[b], Rita Marinelli[a], Gabriele Cruciani[c], Roberto Pellicciari[b], Francesco Galli[a], and Antimo Gioiello[a]

[a] Department of Pharmaceutical Sciences, University of Perugia, Via Elce di Sotto 1, Perugia 06123, Italy; [b] TES Pharma, Taverne di Corciano, Perugia 06073, Italy; [c]Department of Chemistry, Biology and Biotechnology, University of Perugia, Via Elce di Sotto 8, Perugia 06123, Italy

Pregnane X receptor (PXR, NR1I2) is a master xenobiotic sensor and a validated target for immune and inflammatory diseases, including cholestatic liver disease, inflammatory bowel disease (IBD), and dyslipidemia [1]. However, ligand promiscuity is a major obstacle in the pharmacological approach to PXR because most of the ligands identified so far modulate other targets and can exhibit toxicity and/or potential off-target effects. Accordingly, the identification of novel and selective PXR modulators to be employed as chemical probes to investigate the molecular circuits and therapeutic relevance of the receptor is highly desired.

Recently, we have reported that the vitamin E analogue garcinoic acid (GA) selectively activates PXR with an EC_{50} of 1.3 μM (Figure 1) [2]. Crystallographic analysis was indicative of GA binding potency which can be explained by the presence of several and stable interactions. Remarkably, in vivo assays demonstrated that both intestinal and liver PXR respond to the agonistic activity of GA, providing a mechanistic support for the use of this natural compound in PXR-related diseases.

In this communication, we report our current efforts directed toward the preparation of GA derivatives with improved potency, molecular properties, and metabolic stability. In particular, we will describe the synthesis and PXR activity of a first set of GA analogues characterized by the bioisosteric substitution of the terminal carboxylic moiety. Results will be analyzed from a structure-activity relationships point of view and selected compounds will be characterized in terms of physicochemical properties, metabolic behavior and in vivo appraisals.

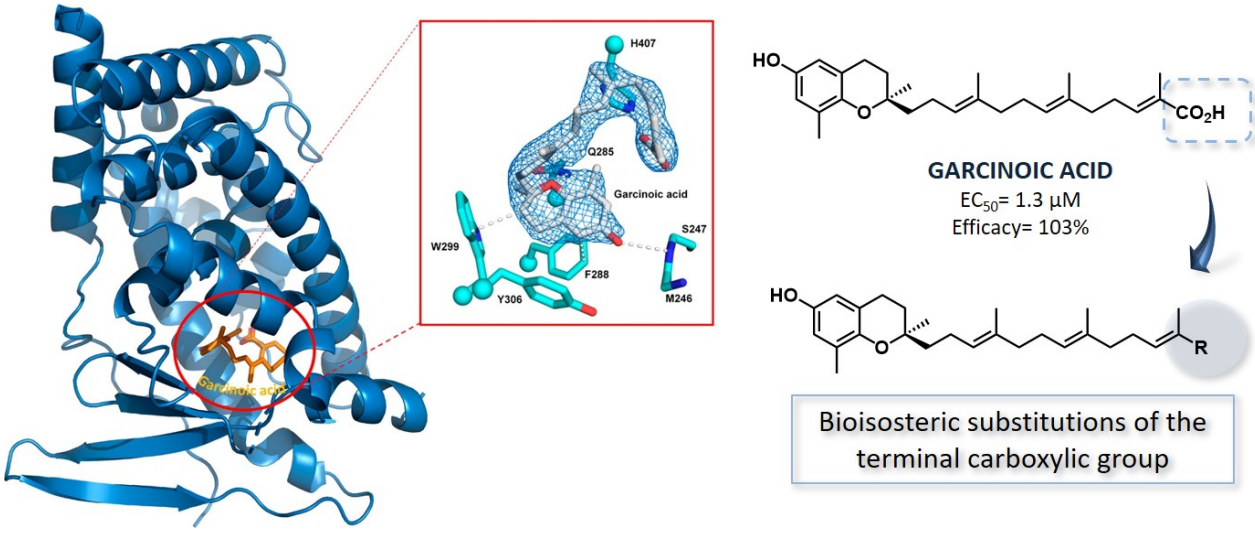

Figure 1. Structure, PXR binding and novel analogues of garcinoic acid.

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Design, synthesis and biological evaluation of deferiprone derivatives as new antimicrobial agents

Tudino V.,[a] Bortolami M.,[b] Pandolfi F.,[b] Messore A.,[c] Rocco D.,[b] Feroci M.,[b] Di Santo R.,[c,d] De Vita D.,[e] Costi R.,[c,d] Cascarino P.,[f] Simonetti G.,[e] Battistoni A.,[a] Scipione L.[c]

[a] Department of Biology, Tor Vergata University of Rome, via della Ricerca Scientifica 1, 00133 Rome, Italy; [b] Department of Basic and Applied Sciences for Engineering, Sapienza University of Rome, via Castro Laurenziano 7, 00161 Rome, Italy; [c] Department of Chemistry and Technology of Drug, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy; [d] Pasteur Institute - Fondazione Cenci Bolognetti, viale Regina Elena 291, 00161 Rome, Italy; [e] Department of Environmental Biology, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy; [f] Department of Public Health and Infectious Diseases, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Rome, Italy

Metals are essential for life and they are indispensable for several biological processes, including precursor biosynthesis, DNA replication, transcription, respiration, and responses to oxidative stress.[1] In the context of infection, metals play a pitoval role within infecting microbes, acting as cofactors in a multitude of enzymes and carrying out roles in virulence signalling and regulation.[2] In particular, many studies reported the role of metals in fungal and bacterial survival and the potential ability of metal chelating agents to interfere with their growth. Amongst them, deferiprone (DFP), an iron chelator approved by FDA for the treatment of transfusional iron overload, was tested towards different strains of *C. albicans*, showing a weak inhibitory activity on fungal growth. Starting from these results, we decided to modify DFP moiety in N1 position, in order to increase its lipophilia, introducing aryl-alkyl groups of different sizes and polarity. We also connected DFP moiety with ketoprofen, ibuprofen or ibufenac respectively, as some authors reported the inhibitory activities of non-steroidal anti-inflammatory drugs (NSAIDs) against *C. albicans*.[3] Compounds **2b** and **3b** resulted chelators of Fe(III) and Cu(II), and showed an interesting activity on planktonic cells (MIC_{50} of 32 ⌈g/mL and 16 ⌈g/mL respectively) and on biofilm formation ($BMIC_{50}$ of 32 ⌈g/mL and 16 ⌈g/mL respectively) in cultured ATCC 10231 *C. albicans*. This activity was reduced, in a concentration dependent way, by the addition of Fe(III) and Cu(II) to the culture media.[3] Some of the most promising compounds were also tested towards wild type and siderophores non-producing mutant strains of *S. typhimurium* and *P. aeruginosa*. Compound **3b** proved to be active, reducing both bacteria growth and inducing iron deficiency.

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Design and synthesis of Larazotide Acetate and derivatives as Potential Anti-SARS-CoV-2 Main Protease Activity

[a] *Maria Carmina Scala,* [a] *Marina Sala,* [a] *Giovanni Vivenzio,* [a] *Alfredo Sica,* [a] *Giuseppe Bifulco,* [a] *Pietro Campiglia,* [b,c] *Alessio Fasano and* [b] *Simone Di Micco*

[a] *Department of Pharmacy, University of Salerno, Via Giovanni Paolo II 132, 84084, Fisciano, Italy;*
[b] *European Biomedical Research Institute of Salerno (EBRIS), Via S. De Renzi 50, 84125 Salerno (SA). Italy;*
[c] *Mucosal Immunology and Biology Research Center, Massachusetts General Hospital–Harvard Medical School, Boston, MA, United States.*

The most severe outcome of COVID-19 infection is the development of interstitial pneumonia causing acute lung injury (ALI) and/or acute respiratory distress syndrome (ARDS), both responsible for the infected patients' mortality [1]. It was previously reported that zonulin, a protein dictating epithelial and endothelial permeability in several districts, including the airways, is involved in ALI pathogenesis in mouse models. In particular, its inhibitor peptide, Larazotide acetate (also called AT1001), currently in phase 3 trials in celiac subjects, ameliorated ALI and subsequent mortality by decreasing mucosal permeability to fluid and extravasation of neutrophils into the lungs.
With the recent crystallographic resolution of the SARS-CoV-2 main protease (Mpro), an enzyme fundamental in the viral lifecycle, bound to peptidomimetic inhibitors N3 and 13b, we were able to perform molecular modeling investigation showing that AT1001 presents structural motifs similar to co-crystallized ligands [2].
Starting from these results, in this work, we synthesized derivatives of AT1001 to rationally improve pharmacokinetic characteristics and binding affinity.

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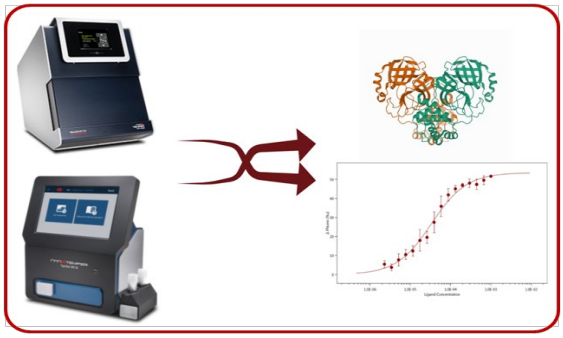
Design of Biophysical Assays for COVID-19 M^{pro}

Elisa Bianconi,[a] Alice Coletti,[b] Deborah Grifagni,[c] Valeria Libera[d], Elisabetta Schiaroli,[e] Lucia Comez,[f] Francesca Cantini,[g] Alessandro Paciaroni,[d] Antonio Macchiarulo.[a]

[a] *Department of Pharmaceutical Sciences, University of Perugia, via del Liceo 1, 06123 Perugia, Italy*
[b] *Department of Medicine and Surgery, University of Perugia, Via Gambuli 1, 06132 Perugia, Italy*
[c] *Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, Sesto Fiorentino, 50019 Italy*
[d] *University of Perugia, Department of Physics and Geology, Perugia, 06123, Italy*
[e] *Infectious Diseases Clinic, Department of Medicine 2, Azienda Ospedaliera di Perugia and University of Perugia, Santa Maria Hospital, Perugia, Italy*
[f] *CNR-IOM c/o Department of Physics and Geology,University of Perugia I-06132 Via Pascoli, Perugia, Italy*
[g] *Magnetic Resonance Center (CERM), University of Florence, via Sacconi 6, Sesto Fiorentino, 50019 Italy*



COVID-19 is a highly infectious disease caused by Severe Acute Respiratory Syndrome Coronavirus 2 (SARSCoV-2) that quickly spread causing a global pandemic.[1] Identification and development of drugs and vaccines is needed for prevention and therapy of this infection. There are many potential drug discovery targets to contrast this disease. One of these is the main protease, (M^{pro} or 3CL^{pro}) which is highly conserved among coronaviruses.[2] This enzyme is an attractive drug target because plays a pivotal role in viral protein processing and it is dissimilar to the human proteases.[3] Therefore, molecules able to specifically bind and inhibit M^{pro} would block viral replication and represent appropriate candidates to develop low-toxicity drugs against this devastating pathogen. In this framework, using drug repurposing approaches, different approved drugs including known antiviral agents have been proposed as M^{pro} inhibitors.
In this communication, we report the design of orthogonal biophysical assays for the characterization of reported M^{pro} inhibitors. Specifically, we used thermal shift analysis and microscale thermophoresis (MST) to evaluate the binding activity of proposed M^{pro} inhibitors including Carmofur, GC-376, Lopinavir, Ritonavir and Nelfinavir. These methods are characterized by a high sensibility and they provided reliable and reproducible data about the nature of the ligand/target interplay. Moreover, to our knowledge, there are no data reported in literature concerning the application of MST to gain insight into the binding profile of M^{pro} inhibitors. Collectively, our results highlight that this protease is a very stable protein and that buffer composition may affect the binding activity of proposed inhibitors. The optimized biophysical assays will be used in screening campaign for the identification of novel more potent M^{pro} inhibitors.

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Effects of mutations on secondary structures of peptides derived from SARS-CoV-2 S/ACE2 binding site: an NMR analysis.

Michela Buonocore[a], Angelo Santoro[a], Manuela Grimaldi[a], Mohammad Firoznezhad[a], Carmen Marino[a], Verdiana Covelli[a], Anna Maria D'Ursi[a]

[a]Department of Pharmacy Università degli studi di Salerno, via Giovanni Paolo II, 132, 84084, Fisciano, Italy

SARS-CoV-2 is a virus belonging to the Betacoronavirus family (Coronaviridae) that causes respiratory disease COVID-19.[1] SARS-CoV-2 infection occurs through the interaction of the viral surface protein Spike (S) with the host's Angiotensin-converting enzyme 2 (ACE2) receptor, which favors the virus's entry into cells and its replication. Viruses, especially RNA viruses such as coronaviruses, constantly evolve through mutations in their genome; accordingly, at least three COVID19 variants have been spread out: UK (B.1.1.7), South African (B.1.351), and Brazilian (P.1) variants, presenting mutations mainly in the Receptor Binding Domain (RBD) and N-terminal domain of the S protein. [2]

To set a system that reproduces the ACE2-S protein binding site and suitable to predict the effect of the mutations on the virus infection, by analyzing the crystal structure of the SARS-CoV-2 S RBD/ACE2 complex (PDB ID: 6M0J)[3], we designed and synthesized a set of peptides mimicking the ^{21}I-Q^{42} ACE2 sequence and ^{482}G-Q^{506} S protein. S protein-derived peptides included the mutated residues: N501Y for UK variant, E484K for South African, and N501Y for Brazilian variants. The peptides were characterized by NMR and CD spectroscopy, and interaction with ACE2 was simulated for each of them by molecular dynamics simulations.

We acknowledge CINECA for awarding us access to Marconi100 within the "COVID-19 Fast access to HPC supercomputing facilities" Call for Proposals organized by Associazione Big Data.

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Convenient enzymatic processing for conversion of food wastes to valuable bioproducts: transformation of picrocrocin to safranal

Giorgia Catinella [a], Martina L. Contente [a], Cecilia Pinna [a], Sabrina Dallavalle [a], Gigliola Borgonovo [a], Andrea Pinto [a]

[a] Department of Food, Environmental and Nutritional Sciences, University of Milan, Via Celoria 2, 20133 Milan, Italy.

Saffron derives from stigmas of flowers of *Crocus sativus L.* and is one of the most expensive spice in the world. [1] The spice is composed of three major secondary metabolites, crocin and its derivatives, picrocrocin and safranal, which give the characteristic color, taste, and odor. [2] Safranal, the principal volatile monoterpene compound, responsible of the intense aroma of saffron, is obtained during the drying process and generated by hydrolysis and dehydration of picrocrocin. [3] A number of beneficial effects are reported for safranal, including neuroprotective properties, antitumoral and anti-depressive activities. [4]

Aiming at recovering the agri-food residues of saffron and transform them into valuable products, a legitimate green choice on the production of precious safranal is the application of biocatalysts. In particular, we have employed the thermo-acidophilic β-glycosidase from *Alicyclobacillus acidiphilus* (AAC) for its ability to hydrolyze very stable glycosidic bonds also in harsh conditions (high temperature, low pH, high substrate loading), as already reported for other natural products. [5]

A two step-reaction was carried out to get the natural precious safranal. Picrocrocin, isolated from the extract of saffron residues, was treated with glycosidase AAC to obtain in 15 min the corresponding aglycone, 4-hydroxy-safranal, with complete conversion. Then, safranal was prepared through a simple acid catalysis.

In this way, also the saffron residues can be reusable and profitable for the recovery of bioactive compounds in a natural way. In fact, in agreement with FDA and EMA regulation, starting from natural material and using biocatalysts, the aroma can be commercialized as natural too, thus increasing its market value.

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UHPLC-MS/MS screening of the hTEAD surface for the identification of novel allosteric inhibitors with anticancer activity

*Lorenzo Tagliazucchi[a], Giulia Malpezzi[a], Cecilia Pozzi[b], Ludovica Lopresti[b], Stefano Mangani[b], Andrea Abdel Latif[a], Glauco Ponterini[a], Alberto Venturelli[a], Maria Paola Costi[a]**

[a] *Department of Life Sciences, Università di Modena e Reggio Emilia, Via Campi 103, 41125 Modena, Italy*
b Dept. of Biotechnology, Chemistry and Pharmacy, Department of Excellence 2018-2022, University of Siena, Via A. Moro 2, 53100 Siena, Italy.

The Hippo signalling metabolic control pathway represents an emerging topic in tumour suppression regulation and regenerative medicine. This pathway, activated by extracellular anti-proliferative signals, is regulated by a cytosolic phosphorylation cascade of four main proteins with serin-threonine kinase activity [1]. At the endpoint of this cascade, phosphorylation of YAP (yes associated protein)/TAZ (Tafazzin) paralogues proteins, act as TEAD1-4 (transcriptional enhancer factor TEF) coactivators. TEAD Ser127 phosphorylation activates YAP/TAZ proteasomal degradation, and this prevents its migration to the nucleus for YAP-TEAD interaction, thus preventing the transcription of genes activating cell proliferation. The hTEAD-4 isoform, the most represented in solid tumor masses, shows three distinct binding surfaces and a lipid pocket, usually occupied by a palmitic/myristic fatty acid forming a thioester with side residue of Cys365 [2]. Despite being a promising pharmaceutical target, the disruption of the YAP-TEAD complex is still under preliminary investigation, and further protein reactivity studies are necessary to better understand how the pathway can be inhibited. Our studies focus on characterizing existing cysteine-based pocket of the hTEAD4-YAP binding domain (YBD) surface by analysing the reactivity of its four cysteine residues (Cys310, Cys335, Cys367, Cys410). These residues are nearby the area where YAP binds but are not fully hindered and therefore show some thiol-like reactivity. As Cys335 is closest to *interface-3,* the region that naturally recognises the YAP Ω-loop sequence, compounds able to interact near this area may suggest novel allosteric binding sites for a new inhibitor class. For this reason, we used UHPLC-HRMS (Orbitrap Q-Ex) and HPLC-UV-ELSD to characterize recombinant hTEAD4, its naturally myristoylated fraction, and its ability to bind a small library of disulphides and thiols with different chemical properties through exposed cysteines residues. Among these ligands, we demonstrated that only a few compounds reacted by forming a disulphide bond. Mass spectrometry ($ddMS^2$) experiment on hTEAD tryptic peptides proved that the ligands display high selectivity towards Cys335. No disulphide is formed with Cys367, not even in the non-myristoylated fraction, probably because of the high lipophilic nature of its pocket. We confirmed the results with an intact protein MS^1 experiment and measured the same mass shift. Ongoing X-ray crystallography experiments will provide the structural bases for an HIT optimization medicinal chemistry program.

Additional ongoing work consists in the exploration of a larger thiophenol-based library by medium throughput MS screening methods, to study the influence of those ligands on the non-covalent interaction of YAP with TEAD. The short-term perspectives of this work are the identification of an allosteric inhibitor useful for YAP-TEAD complex disruption, the confirmation and quantitative assessment of inhibitor binding with an orthogonal assay and the achievement of structural information for starting a hit-optimization medicinal chemistry program.

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The project has been developed in the frame of the Novamolstam regional project.

Development of a Microscale Thermophoresis-based Method for Screening and Characterizing New Ligands of the Methyl Lysine Reader Protein MRG15.

Alessandra Feoli,[a] Vincenzo Pisapia,[b] Monica Viviano,[a] Sabrina Castellano,[a] Tanja Bartoschik,[b] and Gianluca Sbardella.[a]

[a]Department of Pharmacy, Epigenetic Med Chem Lab, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano, SA, Italy.
[b]NanoTemper Technologies GmbH, Flößergasse 4, 81369 Munich, Germany.

MRG15 is a transcription factor containing a chromodomain, an epigenetic methyl-lysine reader protein involved in different physiological and pathological states. [1,2] Despite its involvement in different physio-pathological conditions, to date the role of this protein has not been fully elucidated due to the lack of a specific and potent chemical probe. Hence, we report the development of a microscale thermophoresis (MST)-based assay for the study of MRG15-ligand binding interactions. The assay was developed optimizing labeling conditions, performing assay buffer screening and then validated using a small focused library of small molecule compounds (Figure 1). This library includes molecules previously identified by us as ligands of reader proteins using a "library-on-library" approach as well as derivatives containing methyl-lysine mimetic groups previously reported by us. UNC1215 was tested as the reference compound. This approach yielded to the identification of 10 MRG15 ligands with affinities ranging from 37.8 nM to 59.1 µM. [3] Our method demonstrated to be robust, convenient, and fast and could be applied to other methylation reader domain-containing proteins for the identification of new chemical probes.

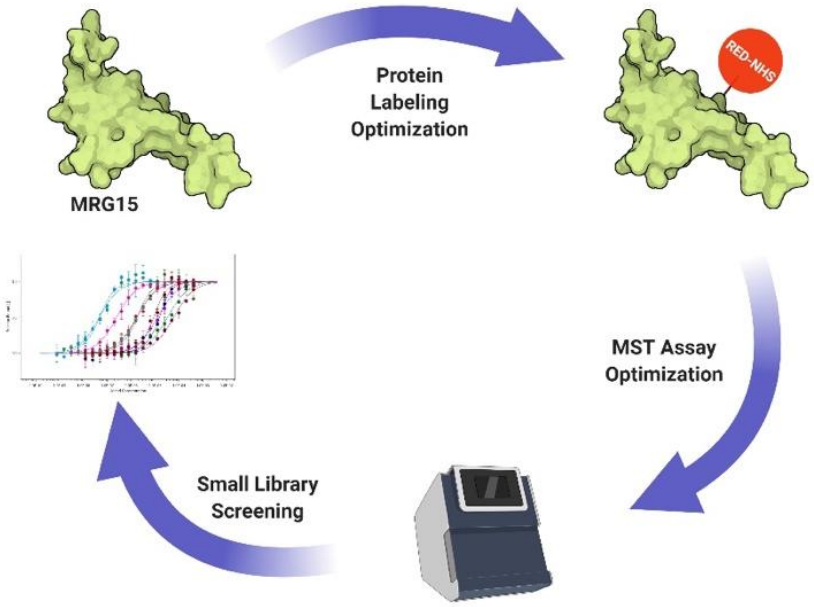

Figure 1: Workflow for the optimization and validation of the MST method

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HPLC-PDA phytochemical evaluation of quinoa seeds grown in different locations

Roberto Mandrioli[a], Lorenzo Marincich[a], Fabiana Antognoni[a]

[a] Department for Life Quality Studies, Alma Mater Studiorum – University of Bologna, Rimini Campus, Corso d'Augusto 237, 47921, Rimini (Italy)

Quinoa (*Chenopodium quinoa* Willd.) is a pseudo-cereal originating from the mountainous zones of South America, whose seeds are widely appreciated for their excellent nutritional profile, especially in terms of essential amino acids, fibre, vitamins, and unsaturated fatty acids. However, more recently quinoa seeds are the subject of intense scientific interest due to their peculiar composition in terms of specialized metabolites with potential health-promoting effects (e.g., phenolic acids, flavonoids, terpenoids, steroids, tocopherols) [1].

Aim of this study was the phytochemical investigation of the content of some polyphenol classes in two different quinoa varieties, the Chilean Regalona-Baer and the Danish Titicaca, grown in three different locations, i.e., Chile, Denmark and Northern Italy. In fact, it is known that the profile of specialized metabolites in Quinoa seeds can vary according to both variables: cultivar and growth location.

After grinding, seeds were extracted in an acidic methanol/water mixture and aliquots were subjected to either basic or acid hydrolysis, in order to determine the free (non-hydrolysed), and soluble-conjugated (basic- or acid-hydrolysed) forms of polyphenols.

The extracts were then subjected to HPLC-PDA analysis under gradient elution, with monitoring at three different wavelengths, for the determination of ten phenolic acids and six flavonoids. In vitro antioxidant activity assays (ABTS, ORAC, FRAP-FZ) were also carried out.

Results indicate that polyphenols are mainly present in all seeds in their soluble-conjugated form. Statistical analysis highlighted just small differences in polyphenol content and antioxidant activity among the four varieties; these differences do not seem to stem from the cultivars, probably because both Regalona and Titicaca are adapted to temperate climates. On the contrary, agro-ecological conditions seem to play a role, however this is relatively small and apparently do not impair overall seed quality when comparing plants grown in Italy to those grown in the zones where the two cultivars come from, i.e. Chile and Denmark, respectively.

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Prenatal and Early Postnatal Cerebral d-Aspartate Depletion Influences l-Amino Acid Pathways, Bioenergetic processes, and Developmental Brain Metabolism

Manuela Grimaldi[a], Carmen Marino[a], Michela Buonocore[a], Angelo Santoro[a], Eduardo Sommella[a], Fabrizio Merciai[a], Emanuela Salviati[a], Arianna De Rosa[b,c], Tommaso Nuzzo[b,c], Francesco Errico[d], Pietro Campiglia[a], Alessandro Usiello[b,c], and Anna Maria D'Ursi[a]

[a]*Department of Pharmacy Università degli studi di Salerno, via Giovanni Paolo II, 132, 84084, Fisciano, Italy*
[b]*Laboratory of Behavioural Neuroscience, Ceinge Biotecnologie Avanzate, 80145 Naples, Italy*
[c]*Department of Environmental, Biological and Pharmaceutical Science and Technologies (DISTABIF), University of Campania, L. Vanvitelli, 81100 Caserta, Italy*
[d]*Department of Agricultural Sciences, University of Naples "Federico II", Via Università, 100-80055 Portici, Italy*

D-Amino acids were believed to occur only in bacteria and invertebrates. Today, it is well known that D-amino acids are also present in mammalian tissues in a considerable amount. In particular, high levels of free D-serine (D-Ser) and D-aspartate (D-Asp) are found in the brain. While the functions of D-Ser are well known, many questions remain unanswered regarding the role of D-Asp in the central nervous system. D-Asp is very abundant at the embryonic stage, while it strongly decreases after birth because of the expression of D-aspartate oxidase (Ddo) enzyme, which catalyzes the oxidation of this D-amino acid into oxaloacetate, ammonium, and hydrogen peroxide. Pharmacologically, D-Asp acts as an endogenous agonist of N-methyl D-aspartate and mGlu5 receptors, which are known to control fundamental brain processes, including brain development, synaptic plasticity, and cognition. In this work, we studied a recently generated knockin mouse model ($R26^{Ddo/Ddo}$), which was designed to express DDO beginning at the zygotic stage. This strategy enables D-Asp to be almost eliminated in both prenatal and postnatal lives. To understand which biochemical pathways are affected by depletion of D-Asp, in this study, we carried out a metabolomic and lipidomic study of Ddo knockin brains at different stages of embryonic and postnatal development, combining nuclear magnetic resonance (NMR) and high-resolution mass spectrometry (HRMS) techniques. Our study shows that D-Asp deficiency in the brain influences amino acid pathways such as threonine, glycine, alanine, valine, and glutamate. Interestingly, d-Asp is also correlated with metabolites involved in brain development and functions such as choline, creatine, phosphocholine (PCho), glycerophosphocholine (GPCho), sphingolipids, and glycerophospholipids, as well as metabolites involved in brain energy metabolism, such as GPCho, glucose, and lactate.

Synthesis and application of ^{13}C labeled carnosine derivatives as internal standards for isotope dilution mass spectrometry measurements in biological matrices

Marco Maspero [a], *Ettore Gilardoni* [a], *Chiara Bonfanti* [b], *Graziella Messina* [b], *Luca Regazzoni* [a], *Marco De Amici* [a], *Marina Carini* [a], *Giancarlo Aldini* [a], *Clelia Dallanoce* [a]

[a] *Department of Pharmaceutical Sciences, Medicinal Chemistry Section "Pietro Pratesi", University of Milan, Via L. Mangiagalli 25, 20133 Milan, Italy;* [b] *Department of BioSciences, University of Milan, Via Celoria 26, 20133 Milan, Italy.*

Carnosine (Figure 1a) is an endogenous dipeptide, composed of β-alanine and L-histidine, highly concentrated in the skeletal muscle and other excitable tissues. It is known for its physiological roles, such as pH-buffering, metal-ion chelation, antioxidant capacity, and the ability to protect against the formation of advanced glycation and lipoxidation end-products.[1] In the past decade, the scientific community was attracted not only by its nutritional ergogenic application [2] but also by its therapeutic potential for the treatment of numerous diseases, in which ischemic or oxidative stress are involved.[1,3] Besides carnosine, most animals also possess the corresponding methylated analogues anserine and/or balenine (Figure 1a). Quantitation of these histidine dipeptides in biological matrices is crucial for their potential applications, and LC-MS procedures with isotope-labeled internal standards are the state-of-the-art approach to this analytical need.[4] The use of these standards allows to overcome variations during complex sample preparation processes, different matrix effects between patient samples, and differences in instrument performance.

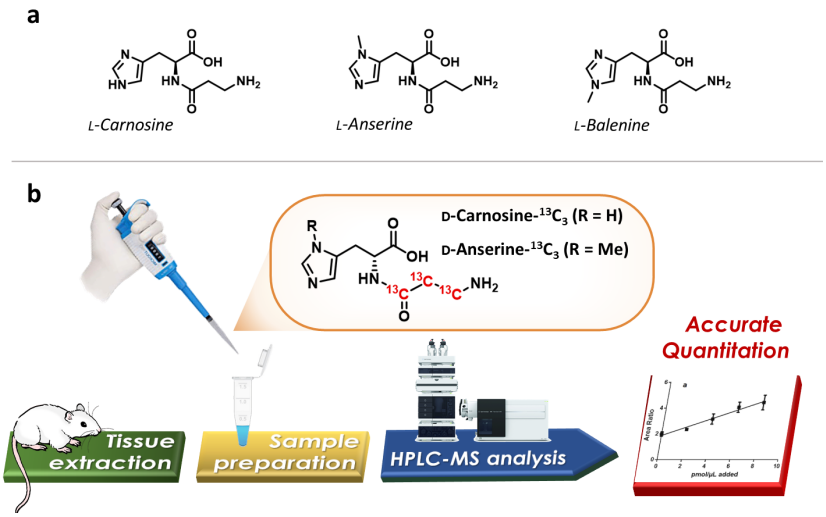

Figure 1: a) Structures of histidine dipeptides, b) ^{13}C-labelled carnosine analogues application.

With this work we present a fast, flexible, and convenient strategy for the synthesis of ^{13}C-labelled carnosine analogues (Figure 1b), and their application as internal standards to the quantitation of carnosine and anserine in a biological matrix.

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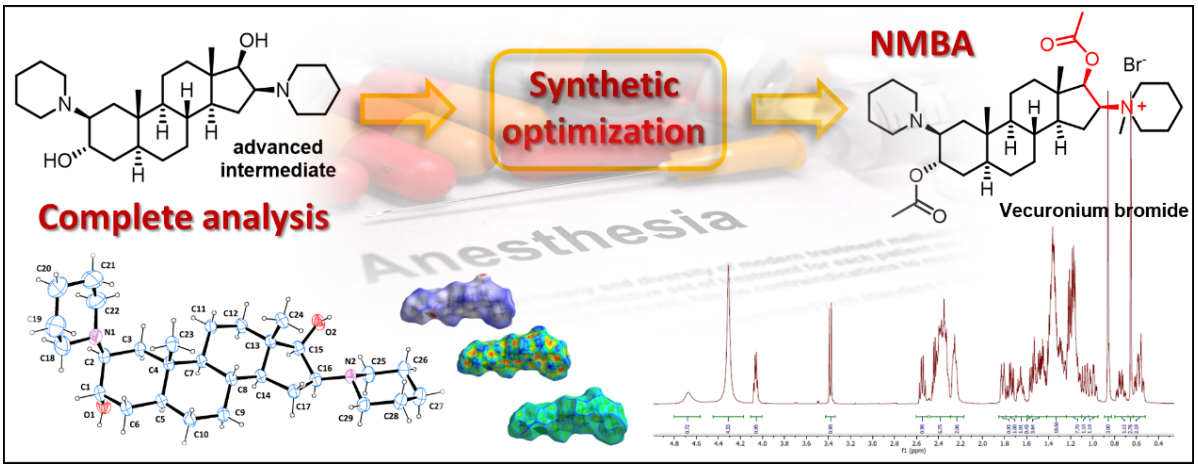
Vecuronium Bromide and its intermediates: a crystallographic and spectroscopic study

Samuele Ciceri [a], Diego Colombo [b], Patrizia Ferraboschi [b], Paride Grisenti [c], Marco Iannone [d], Matteo Mori [a], Fiorella Meneghetti [a]

[a] Department of Pharmaceutical Sciences, University of Milan, Via L. Mangiagalli 25, 20133 Milano, Italy; [b] Department of Medical Biotechnology and Translational Medicine, University of Milan, Via C. Saldini 50, 20133 Milano, Italy; [c] Chemical-Pharmaceutical Consulting and IP Management, Viale G. da Cermenate 58, 20141 Milano, Italy; [d] Department of Medicine and Surgery, Tecnomed Foundation, University of Milano-Bicocca, Monza, Italy

Vecuronium bromide, sold under the brand name Norcuron®, has been extensively used in anesthesiology practice as neuromuscular blocking agent (NMBA) since its launch on the market in 1982.[1,2] However, a detailed crystallographic and NMR analysis of its advanced synthetic intermediates is still lacking. Hence, with the aim of filling this literature gap, vecuronium bromide was prepared starting from the commercially available 2α,3α:16α,17α-diepoxy-5α-androstane, implementing small modifications to a traditional synthetic procedure. A careful NMR study allowed the complete assignment of the ^{1}H, ^{13}C, and ^{15}N NMR signals of vecuronium bromide and its synthetic intermediates. The structural and stereochemical characterization of 2β,16β-dipiperidino-5α-androstane-3α,17β-diol, the first advanced synthetic intermediate carrying all the stereocenters in the final configuration, was described by means of single-crystal X-ray analysis, allowing a detailed conformational investigation.



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Fentanyl pharmacokinetic study for genetic polymorphisms correlation in cancer patients

S. Montanari[a], A. De Simone[b], L. Davani[a], M. Ricci[c], V. Andrisano[a]

[a]*Department for Life Quality Studies, University of Bologna, Corso D'Augusto 237, 47921 Rimini, Italy;*
[b]*Department of Drug Science and Technology, University of Torino, via P. Giuria 9, 10125 Torino, Italy;*
[c]*Palliative Care Unit, IRCCS IRST Dino Amadori, Meldola, (FC), Italy.*

According to international guidelines, fentanyl, a synthetic μ-opioid, is approved for the management of pain in cancer patients. Thanks to its highly lipid solubility and low molecular weight, fentanyl has fast onset of action due to tissue uptake and it can be administered through a patch. [1]
From a pharmacokinetic point of view, fentanyl demonstrates a broad inter-individual variability due to the polymorphism of CYP3A that is responsible for its metabolism. In particular, CYP3A5 polymorphism is a key point in fentanyl adverse effects such as gastrointestinal dysfunction, delirium and respiratory depression. In addition, P-Glycoprotein ABCB1 controls the passage of fentanyl through the blood brain barrier, therefore its polymorphism could be responsible of diverse pain perception and symptoms such as respiratory ones. [2]
In order to find a correlation between fentanyl action on pain and genetic polymorphisms in different cancer patients, the pharmacokinetic characterization of the drug becomes essential.
Therefore, a gas chromatographic–mass spectrometric (GC–MS) analytical procedure has been developed and validated for the determination of fentanyl in human blood.
The sample preparation consisted of a liquid-liquid extraction. The analysis were carried out with Agilent 7820A series gas chromatograph equipped with a 5977E series mass selective single quadrupole detector (MSD) in electron impact (EI) mode (70 eV), under a temperature gradient elution. The limit of detection (LoD) and the limit of quantification (LoQ) values were found to be 0.5 nM and 2.0 nM respectively. The validated method resulted selective and sensitive, suitable to the final goal of this work. Fifty blood samples from cancer patients treated with transdermal fentanyl were collected at fixed intervals during an overall exposure time of 72 hours. The analysis of data and the pharmacokinetic parameters revealed dissimilar pharmacokinetic profiles in the patients examined. Patients were therefore grouped in three categories representing the different trends observed: fast, medium and slow metabolizers. These preliminary data provide significant outcomes for a correlation to clinical response as well as to individual genetic variability.

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Best focusing for drug delivery with composite shape NdFeB magnetic lenses

Alexander Omelyanchik[a,b], Gianrico Lamura[c], Davide Peddis[a,d], Fabio Canepa[a,c]

[a] *Università di Genova, Dipartimento di Chimica e Chimica Industriale, nM2-Lab, Via Dodecaneso 31, I-16146, Genova, Italy*
[b] *Immanuel Kant Baltic Federal University, Kaliningrad, Russia*
[c] *CNR-SPIN, Corso Perrone 24, I-16152, Genova, Italy*
[d] *Istituto di Struttura della Materia, CNR, 00015 Monterotondo Scalo, (RM) Italy*

In the last years, functionalized monodomain Magnetic NanoParticles (MNPs) as carriers for magnetic drug delivery have been extensively studied as a promising agents against several types of cancer [1]. However, while exhaustive researches on the MNPs synthesis and functionalization for drug delivery have been carried out, relatively few studies have been performed on the optimal magnetic field and magnetic gradient parameters required to transport and accumulate the nanoparticles in the targeted organ [2].

We propose a new concept of magnetic focusing for targeting and accumulation of functionalized MNPs in living organs through composite configurations of different permanent magnets [3]. The proposed setups fulfill two fundamental requirements for *in vivo* experiments: 1) reduced size of the magnets to best focusing on small areas representing the targeted organs of mice and rats and 2) maximization of the magnetic driving force acting on the magnetic nanoparticles dispersed in blood. To this aim, several configurations of permanent magnets organized with different degrees of symmetry have been tested. The product $B \cdot grad(B)$ proportional to the magnetic force has been experimentally measured, over a wide area (20×20 mm^2), at a distance corresponding to the hypothetical distance of the mouse organ from the magnets.

Our results give evidence that the magnetic force is maximized by a subtle balance between the polarity configuration and the geometric shape of the used magnets. In particular, we found that, over the typical mice organ size, the average product $B \cdot grad(B)$ attains 10^5 G^2/mm with a mixed configuration of cylindrical and cubic shaped magnets with one of the cylindrical magnet groups with opposite polarity respect to the others. In vivo experiments are in progress to validate our experimental achievements.

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Buffalo milk α_{S1}casein-derived novel peptide protects from angiotensin-evoked high blood pressure

G. Pepe [a], M.G. Basilicata [a], A. Carrizzo [b,c], M. Ciccarelli [b], P. Di Pietro [b], C. Vecchione [b,c], P. Campiglia [a]

[a] Department of Pharmacy, University of Salerno, 84084 Fisciano, SA, Italy; [b] Department of Medicine and Surgery, University of Salerno, 84081 Baronissi, SA, Italy; [c] IRCCS Neuromed, Vascular Pathophysiology Unit, 86077 Pozzilli, IS, Italy.

Endothelial dysfunction and oxidative stress have been implicated in the development of arterial hypertension (AH). In physiological conditions, reactive oxygen species (ROS) play an important role in endothelium-dependent functions while the unbalance between the free radical production and antioxidant systems determines vascular dysfunction [1]. In detail, Angiotensin II (Ang II), the active peptide of the renin-angiotensin system (RAS), exerts a potent and acute vasoconstrictive effect and chronic cardiovascular remodelling [2-4], mainly mediated by its interaction with Ang II type 1 receptor (AT1R) and subsequent activation of NADPH oxidases [3].
In order to prevent and counteract endothelial dysfunction, intake of food-derived antioxidants may protect from oxidative stress and tissue damage. In this contest, buffalo milk dairy products are important dietary components that contribute to the total intake of antioxidants as they release bioactive peptides during gastrointestinal digestion.
For this why, in this study we investigated the possible direct vascular effects of the novel αS1-peptide, namely PG1 (QKEPM), that was obtained at higher concentration after simulated gastro intestinal digestions of buffalo ice-cream sample [5]. In particular, after investigated *in vitro* its bioaccessibility, bioavailability and biotrasformation, the effects of PG1 peptide have been investigated in *ex vivo* by vascular reactivity studies performed on mice mesenteric arteries and *in vivo* on Angiotensin II-treated mice. Our results showed that the PG1 peptide owns potent vascular effect in counteract the effects of angiotensin II-evoked vasoconstriction and high blood pressure levels. The effects of pentapeptide are mediated by the inhibitory effect on AT1 receptor leading to a downregulation of p-ERK12/Rac1-GTP and consequent reduction of oxidative stress. These results strongly candidate PG1, as a novel bioactive peptide for the prevention and management of hypertension.

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Microsampling-based analytical investigation on *in vitro* models of AGC1 deficiency hypomyelination

Michele Protti [a], *Francesco Massimo Lasorsa* [b], *Barbara Monti* [c], *Laura Mercolini* [a]

[a] *Research Group of Pharmaco-Toxicological Analysis (PTA Lab), Department of Pharmacy and Biotechnology (FaBiT), Alma Mater Studiorum - University of Bologna, Via Belmeloro 6, 40126 Bologna, Italy;* [b] *Institute of Biomembranes, Bioenergetics and Molecular Biotechnologies IBIOM, CNR, Via Giovanni Amendola, 122, 70126 Bari, Italy;* [c], *Department of Pharmacy and Biotechnology (FaBiT), Alma Mater Studiorum - University of Bologna, Via Selmi 3, 40126 Bologna, Italy*

AGC1 deficiency is a rare genetic disease leading to a severe encephalopathy in early childhood, caused by mutations in specific genes encoding for the mitochondrial aspartate/glutamate carrier isoform 1 (AGC1). Patients affected by AGC1 deficiency show arrested psychomotor development, seizures, cerebral atrophy and global hypomyelination. In fact, AGC1 has an essential role in regulating the proliferation of neuron-precursor cells (NPCs) and oligodendrocyte-precursor cells (OPCs) [1], as well as in sustaining *N*-acetylaspartate synthesis, potentially explaining the primary clinical symptoms observed in patients. The main aim of this collaborative research project is to investigate and elucidate molecular, epigenetic and biochemical mechanisms altering the myelination/remyelination processes at the basis of the disease onset and progression by exploiting *in vitro* models of the disease. To this purpose, murine NPCs and OPCs have been differentiated from neural stem cells isolated from AGC1+/+ and AGC1+/- mice, while human NPCs and OPCs have been obtained from healthy individuals and AGC1 deficiency patients. From the bioanalytical point of view, the biological and chemical picture of the investigated cells is being complemented by an advanced instrumental analytical approach for metabolite identification and quantitation. Original high-resolution mass spectrometry approaches, also coupled to liquid chromatography (UHPLC-HRMS), have been combined to miniaturised sampling and pretreatment procedures, in order to design, develop, validate and apply this analytical strategy to determine the intracellular content of metabolites involved in glycolysis, tricarboxylic acid (TCA) cycle, malate-aspartate shuttle (MAS) and glutaminolysis, as well as of nucleotides, being aspartate a specific precursor. In fact, reduced sample volumes, solvents and reagents in the framework of sustainable protocols, make advanced miniaturised sampling and pretreatment particularly attractive [2]. A novel miniaturised sample collection and pretreatment workflow has been developed based on microsamples obtained from both cell pellets and culture media, and coupled to an original UHPLC-HRMS method for reliable quali-quantitative evaluations. This approach has been fully validated on a wide set of endogenous biomarkers, obtaining promising results in terms of sensitivity, extraction yields (>84%), precision (RSD<6.9%) and accuracy (>87%). The developed method is promising for the determination of a broad panel of endogenous compounds in miniaturised biosamples. Within this multidisciplinary project the methodology has been applied for the analysis of miniaturised samples coming from *in vitro* murine models and will allow the comparative assessment of biochemical processes involved in AGC1 deficiency. This will in turn clarify altered biochemical pathways in appropriate models of NPCs and OPCs with reduced or abolished AGC1 activity, thus potentially highlighting the presence of specific biomarkers that could play a role in the onset and progression of the disease and address promising therapeutic targets.

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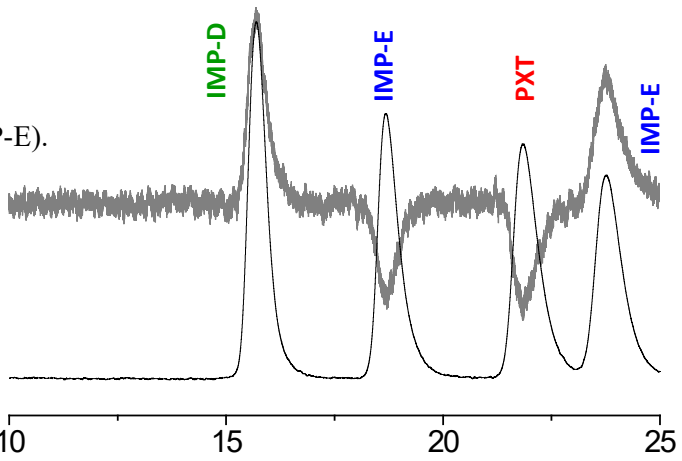
Simultaneous enantio- and diastereo-selective HPLC separation of paroxetine on an immobilized amylose-based chiral stationary phase under green reversed-phase conditions

Alessia Rosetti[a], *Rosella Ferretti*[b], *Claudio Villani*[a], *Marco Pierini*[a], *Roberto Cirilli*[b]

[a] *Department of Chemistry and Technology of Drugs, University ''La Sapienza'', P.le Aldo Moro 5, 00185, Rome, Italy*
[b] *National Centre for the Control and Evaluation of Medicines, Chemical Medicines Unit, Istituto Superiore di Sanità (ISS), Viale Regina Elena 299, 00161, Rome, Italy*
email: alessia.rosetti@uniroma1.it

Paroxetine (PXT) is a phenylpiperidine derivative known to be a potent and selective serotonin reuptake inhibitor (SSRI) of second generation [1]. Due to the presence of two strereogenic centers at C3 and C4, PXT is chiral: of the four possible stereoisomers, only the (3*S*,4*R*) form is active as antidepressant whereas the (3*R*,4*S*) enantiomer (IMP-D) and the diastereoisomeric pair of enantiomers (*3R,4R/3S,4S*) (IMP-E) are its impurities both in the active pharmaceutical ingredient (API) and in the finished product [2]. In the European Pharmacopoeia (EP) for the API PXT hydrochloride hemihydrate an enantioselective reversed-phase HPLC method able to separate PXT from its enantiomer (3*R*,4*S*) (IMP-D) is described [3]: the direct enantioselective separation is achieved on a chiral stationary phase (CSP) based on the a_1-acid glycoprotein (Chiral-AGP) [4,5]. Literature surveys have revealed that actually nothing has been reported concerning the ability of this or other commercially available CSPs to separate the IMP-E enantiomers. So, the aim of the present work is to provide a chromatographic tool for the simultaneous separation of four stereoisomers of PXT. A simple and green high-performance liquid chromatography (HPLC) method for the separation of paroxetine from its enantiomeric and diastereomeric impurities has been developed. The simultaneous chromatographic resolution was carried out on the amylose-based Chiralpak IA-3 chiral stationary phase using the mixture ethanol-water-diethylamine 80:20:0.1 (v/v/v) as a mobile phase [**Fig.1**]. The effects of substitution of ethanol with methanol or acetonitrile and changes in column temperature on specificity have been carefully investigated, allowing the baseline separation of the enantiomers of paroxetine without suffering from interference from other five chiral and achiral impurities reported in its monograph.

Fig.1
The single-run separation of PXT, its enantiomer (IMP-D) and the diastereomers (IMP-E).



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NMR study of peptides interacting with Aβ(1-42) from anti-Aβ monoclonal antibodies

*A. Santoro[a], M. Grimaldi[a], I. Stillitano[a], M. Buonocore[a], A. Gloria[b], A.M. D'Ursi[a]**

[a] *Department of Pharmacy, University of Salerno, Via Giovanni Paolo II, 132 - 84084 Fisciano, Salerno, Italy*
[b] *Institute of Polymers, Composites and Biomaterials, National Research Council of Italy, V.le J.F. Kennedy 54 - Pad. 20, Mostra d'Oltremare, 80125 Naples, Italy*

Alzheimer's disease (AD) is the most common neurodegenerative disorder of the aging population resulting in progressive cognitive and functional decline. Senile plaques, the consequence of the overproduction and/or impaired clearance of β-peptides (Aβ), are considered the hallmark of AD.[1-2] The main components of amyloid plaques are Aβ (1–40) and Aβ (1–42), soluble peptides that, in response to environmental factors, aggregate forming soluble oligomers, protofibrillar oligomers, and finally, insoluble fibrils. Thousands of molecules have been screened as possible drug candidates capable of interacting with Aβ peptide to reduce its toxicity.[3]

Moreover, neutralizing toxic Aβ peptides using anti-Aβ monoclonal antibodies is being pursued as therapies for AD, as growing evidence suggests that passive immunization against Aβ can provide clinical benefit and perhaps AD prevention.[4] Several monoclonal antibodies have been experimented to target different epitopes of the Aβ peptide.

Here we report the design, synthesis, and structural analysis of new ligands of Aβ(1-42) designed on the model of the binding sites of solanezumab[5] and crenezumab[6] binding the central region of Aβ (1-42) and aducanumab[7] binding the N-terminal region. The designed peptides were analyzed for their interaction with Aβ(1-42) using CD and NMR spectroscopies; their effect on the Aβ(1-42) aggregation was studied using atomic force microscopy.

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Edaravone inhibits the formation of neurotoxic metabolite quinolinic acid. A new potential mechanism for the design of neuroprotective agents for the treatment of Amyotrophic Lateral Sclerosis.

Ines Sanz[1], V. Valsecchi[2], L. Mercolini[3], C. Volpi[4], Luca Regazzoni[1]*

[1]*Department of Pharmaceutical Sciences, University of Milan, Via Mangiagalli 25, 20133, Milan, Italy*

[2]*Department of Neuroscience and Reproductive and Odontostomatological Sciences, University of Naples Federico II, Via Pansini 5, 80131, Naples, Italy*

[3]*Department of Pharmacy and Biotechnology (FaBiT), Alma Mater Studiorum - University of Bologna, Via Belmeloro 6, 40126, Bologna, Italy*

[4]*Department of Medicine and Surgery, University of Perugia, Via Gambuli 1, 06132, Perugia, Italy*

** Email:ines.sanz@unimi.it*

Edaravone (3-methyl-1-phenyl-2-pyrazolin-5-one, Radicava®) is one of the two drugs approved for the treatment of Amyotrophic Lateral Sclerosis (ALS), a fatal neurodegenerative disease caused by death of motor neurons both in the cortex and in the spinal cord. The mechanism of action of the compound is likely due to a combination of antioxidant and radical scavenging properties, along with a modulation of Nrf2/HO-1 pathway [1].

Interestingly, edaravone have been recently described also as a good scaffold for drug design of analogs and conjugates with diverse pharmacological properties [2].

Despite an exhaustive literature about antioxidant and anti-radical activities, a neglected property of edaravone is its reactivity against unsaturated aldehydes generated by lipid peroxidation [3].

We hypothesize that edaravone can bind also (2Z,4Z)-2-amino-3-carboxymuconate 6-semialdehyde (ACMS), which is structurally similar to lipid peroxidation aldehydes but generated by tryptophan catabolism and specifically by 3-hydroxyanthranilate 3,4-dioxygenase (HAAO, EC:1.13.11.6). Such a mechanism can be relevant in ALS treatment since ACMS undergo spontaneous cyclization to generate quinolinic acid (QUIN), a neurotoxic metabolite inducing disease progression [4].

To test such a hypothesis, we setup a sensitive method to measure the enzymatic activity of HAAO by means of liquid chromatography-tandem mass spectrometry (LC-MS). Enzyme activity was measured by monitoring the consumption of the substrate (3-hydroxyanthranilic acid) induced by either recombinant HAAO or mouse brain homogenate. In view of future animal studies, the method was designed to allow the screening of potential enzyme inhibitors *in vitro* and *ex vivo*, and to use little amount of substrate and enzyme.

Concerning HAAO activity, the method gave results comparable with published data, whereas the novelty was the demonstration that edaravone inhibits the formation of QUIN generated by the enzyme. Interestingly, the activity of edaravone was retained also in mouse brain homogenate, thus demonstrating that HAAO inhibition can be a further mechanism contributing to the overall efficacy of edaravone in ALS treatment.

These findings open new perspectives for HAAO as potential drug target for the design and test of selective inhibitors based on edaravone scaffold.

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Overcome chemoresistance: biophysical and structural analysis of synthetic FHIT-derived peptides

[a] Maria Carmina Scala, [b] Simone Di Micco, [c] Delia Lanzillotta, [a] Giuseppe Bifulco, [c] Francesco Trapasso, [a] Pietro Campiglia and [a] Marina Sala

[a]Department of Pharmacy, University of Salerno, Via Giovanni Paolo II 132, 84084, Fisciano, Italy;
[b]European Biomedical Research Institute of Salerno (EBRIS), Via S. De Renzi 50, 84125 Salerno (SA). Italy;
[c]Department of Experimental and Clinical Medicine, University Magna Græcia, Campus S. Venuta, via Europa 88100, Catanzaro, Italy.

The fragile histidine triad (FHIT) protein is a member of the large and ubiquitous histidine triad (HIT) family of proteins. On the basis of genetic evidence, it has been postulated that the FHIT protein may function as tumor suppressor, implying a role for the FHIT protein in carcinogenesis. Recently Gaudio et al. reported that FHIT binds and delocalizes annexin A4 (ANXA4) from plasma membrane to cytosol in paclitaxel-resistant lung cancer cells, thus restoring their chemosensitivity to the drug. They also identified the smallest protein sequence of the FHIT still interacting with ANXA4, ranging from position 7 to 13: QHLIKPS [1]. This short sequence of FHIT protein was not only able to bind ANXA4 but also to hold its target in the cytosol during paclitaxel treatment, thus avoiding ANXA4 translocation to the inner side of cell membrane. Starting from these results, to obtain much information about structure requirements involved in the interaction of the peptide mentioned above, we synthetized a panel of seven peptides through an Ala-scan approach. In details, to study the binding of FHIT derived peptides with ANXA4, we applied a combination of different biophysical techniques such as differential scanning fluorimetry (DSF), surface plasmon resonance (SPR), microscale thermophoresis (MST). Circular Dichroism (CD) and nuclear magnetic resonance (NMR) were used to determine the conformational structure of the lead peptide (7-13) and peptides generated from ala-scan technique.
The application of different biophysical and structural techniques, integrated by a preliminary biological evaluation, allowed us to build a solid structure activity relationship on the synthesized peptides.

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Potential antidiabetic effect of the Spirulina peptide SP6: A metabolomics and lipidomics approach

[a, b]Alfredo Sica, [a, b]Fabrizio Merciai, [a]Marina Sala, [a]Maria Carmina Scala, [a, c, d]Albino Carrizzo, [a]Emanuela Salviati, [a, c, d]Carmine Vecchione, [a]Eduardo Sommella, [a]Pietro Campiglia

[a] Department of Pharmacy, University of Salerno, Fisciano, SA, Italy;
[b] PhD Program in Drug Discovery and Development, University of Salerno, Fisciano, SA, Italy;
[c] Department of Medicine and Surgery, University of Salerno, Baronissi (SA), Italy;
[d] IRCCS Neuromed, Loc. Camerelle, Pozzilli (IS), Italy

According to recent estimates, the human population worldwide appears to be in the midst of an epidemic of diabetes. Although several new drug therapies have been developed, such as (GLP-1) receptor agonists, DPP-4 inhibitors, and (SGLT2) inhibitors, to date there is still an extreme difficulty in obtaining adequate metabolic control of patients with type 2 diabetes. Hence, novel therapeutical agents as well as the comprehension of their mechanism are needed. Recently, through simulated gastro-intestinal-digestion (GID) of microalgae spirulina platensis we have identified a novel decameric peptide, namely SP6 (GIVAGDVTPI), which is able to induce a direct *in vivo* vasorelaxant effect through PI3K/Akt/eNOS pathway and deeply modulate lipid metabolism [1, 2]. Furthermore, in a mouse model of pre-diabetes, SP6 was able to reduce blood glucose levels, thus paving the way to further studies. For this purpose, in this work a comprehensive metabolomic and lipidomic profile was performed by multiple mass spectrometry approaches. Polar metabolites and lipids were profiled in plasma, liver and pancreas. Results highlighted a deep modulation of several metabolite classes, such as glycerolipids, aminoacids, nucleotides, and thus numerous key molecular pathways. The obtained results will be useful to understand the potential employment of SP6 peptide in type 2 diabetes management.

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Chemical Investigation and Screening of Anti-Proliferative Activity on Human Cell Lines of Pure and Nano-Formulated Lavandin Essential Oil

Elisa Ovidi [1], Valentina Laghezza Masci [1] , Anna Rita Taddei [2] , Patrizia Paolicelli [3] , Stefania Petralito [3] , Jordan Trilli [3] , Fabio Mastrogiovanni [1] , Antonio Tiezzi [1] , Maria Antonietta Casadei [3] , Pierluigi Giacomello [3] and Stefania Garzoli [3]

1 Department for the Innovation in Biological, Agrofood and Forestal Systems, Tuscia University, 01100 Viterbo Italy;

2 High Equipment Centre, Tuscia University, 01100 Viterbo, Italy;

3 Department of Drug Chemistry and Technology, Sapienza University, 00185 Roma RM, Italy;

Essential oils (EOs) are obtained from different parts of aromatic plants such as flowers, leaves, rhizomes, seeds, wood, fruits and bark. EOs are a complex mixture rich in volatile molecules, which varies in quantity and quality according to exogenous and endogenous factors [1]. Among them, lavandin essential oil (LEO), a natural sterile hybrid obtained by crossbreeding L. angustifolia × L. latifolia, is mainly composed by active components belonging to the family of terpenes endowed with relevant anti-proliferative activity. Unfortunately, pharmaceutical application of LEO is greatly limited by poor physico-chemical properties, including limited water solubility, which requires the production of an adequate formulation in order to overcome poor biopharmaceutical properties an fully exploit their therapeutic [2]. Among all the suitable formulation strategies, aqueous nanoemulsions are gaining increasing interest; they are ultrafine isotropic dispersed systems of two non-miscible liquids, generally consisting of an oily phase dispersed in an aqueous one, in the form of nanometer-sized droplets stabilized by an interfacial film of surfactant. The solvent displacement method was used for the fabrication of an o/w nanoemulsion as delivery system for lavandin essential oil (LEO). It involves a solvent evaporation step, which may lead to volatilization and/or degradation of EO, thus influencing its final composition and functional properties. For this purpose, headspace (HS) extraction system coupled with a GC/MS was performed in order to verify eventual qualitative and quantitative differences [3]. The antiproliferative activity of LEO on several human tumor cell lines including human neuroblastoma cells (SHSY5Y), human breast adenocarcinoma cells (MCF-7), human lymphoblastic leukemia cells (CCRF CEM), human colorectal adenocarcinoma cells (Caco-2) and one normal breast epithelial cell (MCF10A), was investigated by the MTT (3-(4,5-Dimethylthiazol-2-yl)-2,5-Diphenyltetrazolium Bromide)-assay. The chemical composition and the activity exerted by the oil formulated in nanoemulsion (NanoLEO) on the same cell lines were also investigated to compare the biological effects with pure LEO. For this purpose, scanning and transmission electron microscopy investigations (SEM and TEM) were also carried out to outline at ultrastructural level possible affections induced by LEO and NanoLEO treatments. In particular, LEO and its formulation (NanoLEO) analyzed by HS/GC-MS (Headspace/Gas Chromatography-Mass Spectrometry) showed that the most abundant compounds were linalool and 1,8-cineole (LEO: 28.6%; 27.4%) (NanoLEO: 60.4%; 12.6%) followed by α-pinene (LEO: 9.6%; NanoLEO: 4.5%), camphor (LEO: 6.5%; NanoLEO: 7.0%) and linalyl acetate (LEO: 6.5%; NanoLEO: 3.6%). The cytotoxic effects of LEO investigated on different human tumor cells lines showed that Caco-2, MCF7 and MCF10A normal cells resulted more resistant to the treatment with LEO, while CCRF-CEM and SHSY5Y cells were more sensitive. Further, the antiproliferative effect of LEO resulted amplified when the essential oil was supplied as nanoformulation (NanoLEO), mainly in Caco-2 cells. Scanning and transmission electron microscopy investigations were carried out on Caco-2 cells to outline at ultrastructural level possible affections induced by LEO and NanoLEO treatments.

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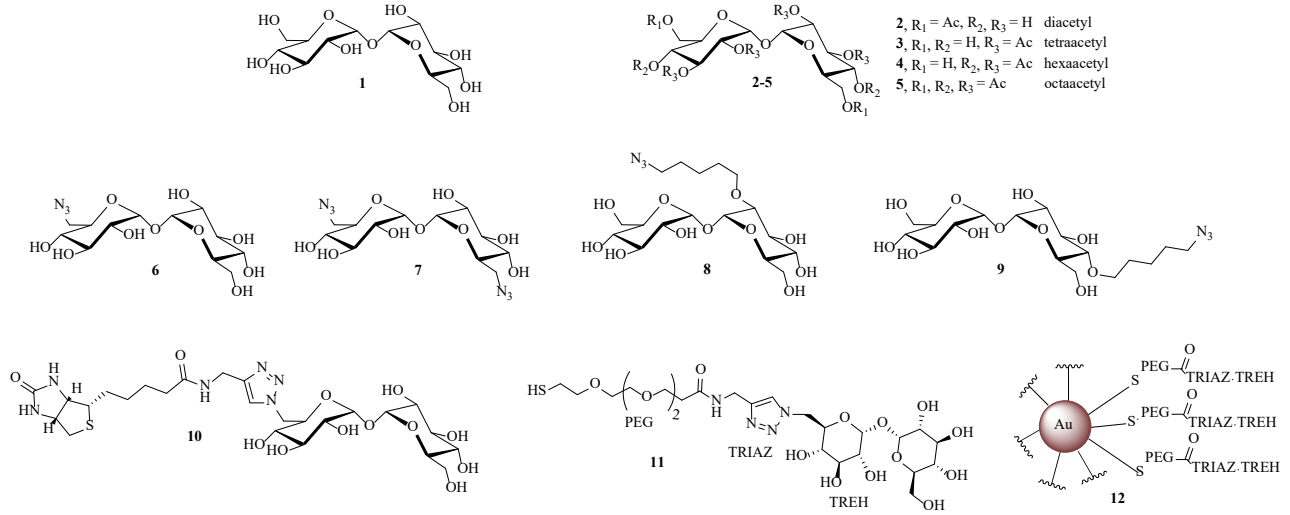
Trehalose-based neuroprotective autophagy inducers

Giulia Assoni[a], Giulia Frapporti[a], Eleonora Colombo[b], Davide Gornati[b], Maria Dolores Perez-Carrion[c], Laura Polito[d], Pierfausto Seneci[b], Giovanni Piccoli[a], Daniela Arosio[d]

[a]Department of Cellular, Computational And Integrative Biology, (CIBIO), Via Sommarive 9, I-38123 Povo, TN, Italy; [b]Chemistry Department, Università Statale di Milano, Via Golgi 19, I-20133 Milan, Italy; [c]Unidad Asociada Neurodeath, Departamento de Ciencias Médicas, Universidad de Castilla-La Mancha, Albacete, Spain; [d]Istituto di Scienze e Tecnologie Chimiche (SCITEC) "Giulio Natta", Consiglio Nazionale delle Ricerche (CNR), Via C. Golgi 19, I-20133 Milan, Italy and Via G. Fantoli 16/15, I-20138 Milan, Italy

α,α-trehalose (O-α,-D-glucopyranosyl-[1→1]-α-D-glucopyranoside, **1**) possesses unique physical and chemical properties, which make it an attractive ingredient in food, health and beauty, and pharmaceutical products [1].
Recent studies [2] have demonstrated that α,α-trehalose is able to induce autophagy in neural cells, hampering development of diseases that result from the aggregation of anomalous proteins folding, such as ALS, tauopathies, and FTD.
Unfortunately, α,α-trehalose poorly permeates biological membranes, because of its high hydrophilicity. Moreover, higher vertebrates express on their intestinal membrane trehalase enzymes to hydrolyze trehalose to two molecules of glucose, preventing its bioavailability by oral administration. Thus, extremely high dosages are needed for in vivo effects in animals and humans.
For these reasons, we designed and synthesized novel trehalose-based chemical entities with measurable autophagy-inducing properties, and biologically active trehalose-based probes to gather information about its molecular mechanism of action [3]. A small array of trehalose prodrugs (**2-5**), putative probes (**6-10**), and inorganic nanovectors (**12**) will be presented together with the evaluation of their autophagy-inducing properties, bioavailability, and molecular mechanism of action.



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A new series of 2- and/or 5-substituted benzimidazoles as potential inhibitors of nicotinic acid phosphoribosyltransferase (NAPRT)

Baldassarri Cecilia,[a] Del Bello Fabio,[a] Giorgioni Gianfabio,[a] Piergentili Alessandro,[a] Sorci Leonardo,[b] Gasparrini Massimiliano,[b] Cappellacci Loredana,[a] Raffaelli Nadia,[b] Petrelli Riccardo[a]

[a]School of Pharmacy, University of Camerino, 62032 Camerino (Italy); [b]Department of Agricultural, Food and Environmental Sciences. Polytechnic University of Marche, 60131 Ancona (Italy)

Alterations in cell metabolism have emerged as one of the hallmarks of cancer that could lead to new targeted therapeutic approaches. A strong reliance on a sustained biosynthesis of nicotinamide adenine dinucleotide (NAD) is undoubtedly included among these alterations. NAD is an important cofactor in redox reactions of energetic metabolism and a consumable substrate of enzymes regulating key cellular processes, including differentiation, metabolic adaptation, inflammatory response, and signal transduction. NAD regeneration is guaranteed by multiple biosynthetic pathways that start from different precursors, which comprises nicotinamide (NAM), nicotinic acid (NA), and nicotinamide riboside (NR). Four major different biosynthetic pathways contribute to the overall NAD pool, and they can occur in different combinations and with different efficiency. In particular, the synthesis of NAD from NA is under the control of NA phosphoribosyltransferase (NAPRT) that catalyzes phosphoribosylation of NA to nicotinic acid mononucleotide (NAMN). In some types of cells, NAPRT is essential for the NA-induced increase in NAD levels and exerts a protective effect. The *NAPRT* gene is commonly amplified and overexpressed in several types of tumors, including ovarian, pancreatic, liver, and colorectal cancers [1], which is in keeping with the higher demand of cancer cells for NAD, with respect to normal cells. In ovarian and pancreatic cancer cells, NAPRT silencing reduces energy status, protein synthesis, and cell size, indicating the enzyme might represent a promising anti-cancer target. In addition, cancer cells expressing high levels of NAPRT are resistant to NAM phosphoribosyltransferase (NAMPT) inhibitors, a widely recognized anti-cancer approach. Both silencing of *NAPRT* gene and chemical inhibition of NAMPT overcome such resistance, suggesting that co-administration of NAPRT and NAMPT inhibitors might effectively decrease NAD levels, leading to cancer cell death [2]. To date, only a few compounds with a weak inhibitory activity on NAPRT have been identified. For this reason, there is a need for more potent and selective NAPRT inhibitors with improved pharmacokinetic properties.

In this scenario, we screened more than 200 molecules available in our labs and characterized by different chemical scaffolds in order to discover novel chemotypes able to inhibit NAPRT. We identified a hit compound bearing the properly 2- and 5-substituted benzimidazole nucleus, with promising pharmacological and structural characteristics (IC_{50} ~1.5 mM). Based on the chemical structure of this initial hit, we synthesized and characterized a series of structural analogs to develop a comprehensive structure-activity relationship (SAR) investigation and to establish the minimal structural determinants for an efficacious NAPRT inhibition. An optimized lead compound with an improved biological profile (with the IC_{50} at the micromolar level) has been identified, and its potential mechanism of action will be discussed.

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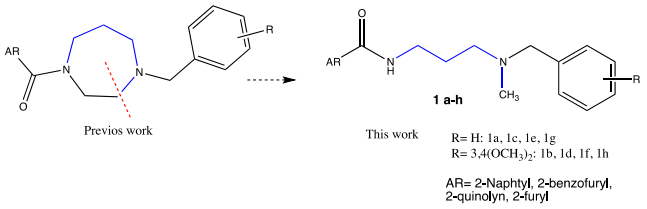
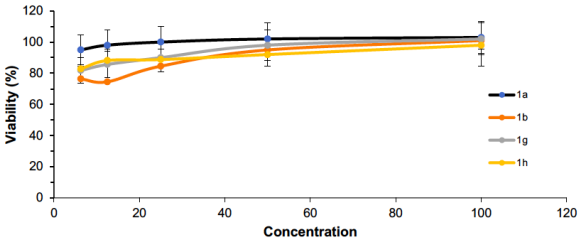
Design, synthesis and biological evaluation of new aminopropylcarboxamide derivatives as sigma ligands

D. Zampieri[a], S. Fortuna[a], V. Costa[a], A. Cassina Temporini[a], S. Tosolini[a], M. Romano[b], E. Amata[c], M. Di Chiara[c], L. Pasquinucci[c], R. Turnaturi[c], A. Marrazzo[c], M.G. Mamolo[a]

[a] Department of Chemical and Pharmaceutical Sciences, Via Giorgieri 1, University of Trieste, 34127 Trieste (I); [b] Department of Life Science, Via Valerio 28/1 University of Trieste, 34127 Trieste (I); [c] Department of Drug and Health Sciences, Viale A. Doria 6, University of Catania, 95125 Catania (I).

The sigma receptors (σR) are a class of proteins initially classified, by Martin and co-workers, as a subtype of the opiate receptors [1]. They are predominantly localized in the CNS as well as in many peripherical organs such as liver, heart and in some types of cancer cells.
Two receptor subtypes have been identified, namely σ1 and σ2 [2-5]. The σ1R, in particular, are therapeutic targets for neurological disorders such as Alzheimer's and Parkinson's diseases, depression and drug addiction, whereas the σ2R subtype are overexpressed in many cancer cells and, in this context, the σ 2R agonists can be potential anticancer agents or can find application as a target of radio-labelled ligands for the identification of solid malignant tumors.
On the basis of our previous work [6] herein we synthesized a small library of aminopropylcarboxamide derivatives having high affinity, for both σR subtypes.





Viability of compounds **1a,1b, 1g** and **1h** against SH-SY5Y cell line

Binding assay towards σRs have been performed towards both receptor subtypes, and the more interesting compounds was found to be the unsubstituted (R= H) quinoline **1a** and the benzofuran **1g** derivatives (AR) which showed a pan affinity towards both receptor subtypes, with Kiσ1= 15.56 and 12.25 nM and Kiσ2= 20.99 and 9.95 nM, respectively. The 3,4-dimethoxy substitution was effective in shifting the affinity towards σ2R subtype, indeed the corresponding quinoline derivative **1b** showed Kiσ2= 16.33 nM *vs.* Kiσ1= 572.80 nM with selectivity index of 35, and the benzofuran derivative **1h** showed Kiσ2= 41.13 nM *vs.* Kiσ1= 374.97 nM and selectivity index of 8. Cytotoxicity data against SH-SY5Y neuroblastoma cell line, showed that none of the compounds examined induces toxic effects, therefore they would promote neuroprotection with plausible σ1 agonist and σ2 antagonist profile.
Antioxidant activity and binding studies towards different receptors are currently ongoing.

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From black mamba snake venom a new potent and selective antagonist of muscarinic type 2 receptor

Lidia Ciccone [a,b,c], *Justyna Ciolek* [b], *Enrico Stura* [b], *Pierre Legrand* [c], *Didier Boturyn*[d], *Guillaume Blanchet*[b], *Philippe Robin*[b], *Gilles Mourier* [b] *and Gilles Nicolas* [b]

[a]*Università di Pisa, Dipartimento di Farmacia, via Bonanno 6, 56126, Pisa, Italia;* [b]*Université Paris Saclay, CEA, INRAE, Département Médicaments et Technologies pour la Santé (DMTS), SIMoS, 91191 Gif-sur-Yvette, France;* [c]*Societé civile Synchrotron SOLEIL, L'orme des Merisiers Saint-Aubin-BP48, Gif-surYvette, 91192, France;* [d]*CNRS UMR 5250, Université Grenoble Alpes, Institut de Chimie Moléculaire de Grenoble, Bâtiment NANOBIO, 38041 Grenoble*

Snake venom is a natural biological resource of several components with potential therapeutic value. The bioactive molecules are metabolites such as small chemical compounds, as well as short peptides and enzymes.

Muscarinic acetylcholine receptors (mAChRs) are members of the G-protein-coupled receptors (GPCRs) superfamily and play an important role in multiple functions of the central and peripheral nervous systems, including in cardiovascular functions [1,2]. The mAChRs are classified in five subtypes. The M1, M4 and M5 receptors are predominantly expressed in neurons and glial cells of the central nervous system, whereas the M2 and M3 subtypes are also distributed in the peripheral tissues where they control the parasympathetic system.

Yet, we often lack selective pharmacological drugs to assess the respective contribution of muscarinic receptor subtypes to a given function. We turned towards mamba snake venoms to identify a selective M2 receptor (M2R) ligand for investigating the contribution of the M2 receptor to arterial contractions.

In our study we have identified a natural peptide MT9 from the black mamba venom.

We synthesized MT9 peptide using solid phase Fmoc chemistry and native chemical ligation. Two peptide fragments, P1 and P2 (TICHIQISKTHGILKTCEENS-NH-NH2, and CYKMSVRGWIIGRGCGCPSAVRPRQVQCCTSDKCNY-OH), were chemically synthesized and purified and ligated to each other to produce reduced MT9 [3].

The peptide structure was solved by X-ray diffraction confirming that MT9 belongs to the three-finger fold toxins family [4].

Functional tests and ex vivo experiments on rat and human arteries MT9 shows high selectivity profile towards M2R versus the four other muscarinic receptors.

MT9 is the first fully characterized M2R-specific natural toxin. MT9 can be considered as a new drug candidate in cardio-vascular diseases.

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Design, synthesis, and in vitro evaluation of bivalent chemical probes targeting the tandem BD1/BD2 in BET proteins

Alessandra Cipriano,[a] Ciro Milite,[a] Sarah Picaud,[b] Panagis Filippakopoulos,[b] Sabrina Castellano,[a] and Gianluca Sbardella.[a]

[a]Epigenetic Med Chem Lab, Dipartimento di Farmacia, Università degli Studi di Salerno, Via Giovanni Paolo II 132, I-84084 Fisciano, Salerno, Italy. [b]Structural Genomics Consortium, Nuffield Department of Clinical Medicine, University of Oxford, Old Road Campus Research Building, Roosevelt Drive, Oxford OX3 7DQ, UK.

One of the most important group of bromodomain-containing proteins is the Bromo and Extra-Terminal Domain (BET) family, whose members (BRD2, BRD3, BRD4, and BRDT) contain two highly homologous bromodomains (BRDs): BD1 and BD2. Through their BRDs, these proteins selectively recognize the acetyl-lysine group on histone and non-histone proteins, acting as epigenetic readers.[1] To date, several compounds have been identified as potent BET ligands. However, the high homology between the acetyllysine-binding pockets within BET members has limited the identification of BD1/ BD2 selective ligands.[2] Nevertheless, several reports indicated that these domains have different functions, demanding the development of isoform-selective ligands to clarify the importance of simultaneous or selective inhibition.[3] Herein, we report the design, the synthesis, and the in vitro evaluation of bivalent chemical probes targeting the tandem BD1/BD2 domains (Figure 1). Exploring different type of linkers, these molecules were obtained merging a triazolobenzotriazepine-based compound (**Cl-BzT-7**) as BD1 ligand and the **RVX-208**, a selective inhibitor of BD2 domain. The aim is to obtain compounds potentially able to bind both BD1 and BD2 bromodomains simultaneously.[4,5]

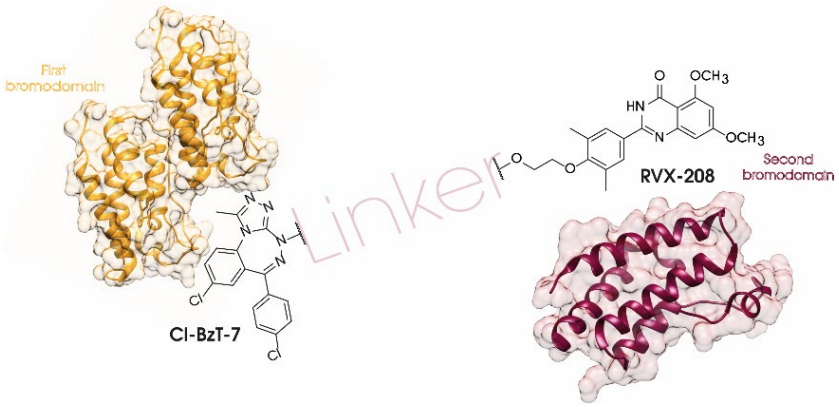

Figure 1. Aim of work: Identification of bivalent chemical probes targeting BD1/BD2 domains.

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Design, synthesis and biological evaluation of MOR agonist/HDACi hybrid compounds: a new potential therapeutic strategy for persistant pain management

Giuliana Costanzo[a], Rita Turnaturi[b], Agostino Marrazzo[b] and Lorella Pasquinucci[b]

[a] Department of Biomedical and Biotechnological Sciences, University of Catania, Via Santa Sofia, 97, 95123,Catania (Italy)
[b] Department of Drug and Health Science, University of Catania, Viale Andrea Doria, 6, 95125, Catania (Italy)

Recently, the Hystone Deacetylase (HDAC) enzyme has been identified as a new target in pain transmission. Literature data suggest that epigenetic regulation is involved in development and maintenance of chronic pain.[1] Indeed, HDACi attenuate both neuropathic and inflammatory pain increasing the expression of HDAC in inflammatory conditions or nerve injury. Moreover, the histones H3 and H4 hypoacetylation contributes to the decreased expression of mu opioid receptor (MOR) in the dorsal root ganglion .[2]
For these reasons, the development of hybrid MOR agonist/HDACi compounds could be a good strategy to increase analgesic efficacy of opioids. In fact, associated administration of HDACi and morphine appreciably delayed the development of morphine tolerance in a persistent pain model.
Hybrid compounds were designed recurring to the "merging" approach.[3]

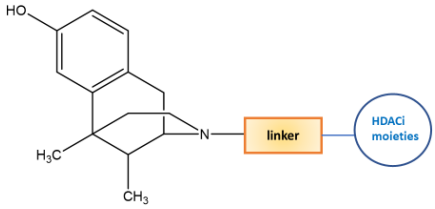

Figure 1: Rational design of MOR agonist /HDACi hybrid compounds.

New hybrid ligands have been synthesized, purified and structurally characterized with ^{1}H NMR ,^{13}C NMR and MS spectra.
In vitro their affinity profile *versus* opioid receptors are performed through competition binding assays. Also, the inhibition properties in HDAC fluorimetric assays further allow to define in vitro profile of our dual target compounds.
The preclinical evaluation of these compounds is ongoing. In vivo evaluation in animal models of inflammatory and neuropathic pain will be programmed.

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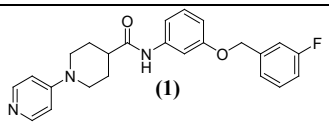
First-in-class isonipecotamide-based thrombin and cholinesterase dual inhibitors with potential for Alzheimer disease

Modesto de Candia, Rosa Purgatorio, Nicola Gambacorta, Marco Catto, Leonardo Pisani, Orazio Nicolotti, and Cosimo D. Altomare

Department of Pharmacy – Drug Sciences University of Bari "Aldo Moro", via Orabona 4, I-70125, Bari

Alzheimer's disease (AD) is a neurodegenerative and devastating disorder, accounting for the most elderly-related dementias. As reported in World Reports, the number of people affected by AD is expected to increase up to 13.4 million in 2030.[1] Nevertheless, few drugs are currently available only for merely symptomatic treatments of mild-to-moderate AD. They include the reversible or pseudoreversible AChE (acetylcholinesterase) inhibitors (i.e., galantamine, donepezil and rivastigmine), and the NMDA (*N*-methyl-D-aspartate) receptor antagonist memantine.
A relevant number of elderly patients affected by AD and dementias reported comorbidities, such as cardiovascular dysfunctions. Vascular and thrombotic risk factors (i.e., hypertension, diabetes, and hyperlipidemia) have been described as potentially associated with the progression of cognitive decline in AD and vascular and mixed dementia.[2]
Recently, the beneficial effects of the well-known clinical available thrombin inhibitor dabigatran have been observed in AD mouse models after long-and short-term administration. Such a treatment resulted in the mitigation of neuroinflammation, reduction of the histopathological AD hallmarks, and recovery of cognitive decline.[3]
Noteworthy, in the last decade we reported the rational identification of several classes of (iso)nipecotamide derivatives able to act as selective thrombin or factor Xa inhibitors by little structural modifications.[4] A pool of these derivatives was thus screened by employing our recently developed MuSSeL web server,[5] in the attempt of finding other putative and clinically relevant targets. Interestingly, some of the screened compounds were flagged as potential binders of attractive protein drug targets, including cholinesterases (electric eel AChE and equine butyrylcholinesterase BChE). Inspired by the paradigm of the MTDL (multi-target drug ligands) design, herein we aimed at integrating in one molecule the potential to bias cholinesterases, on one side, and key coagulation factors, thrombin and fXa, on the other.
In this attempt, the isonipecotamide derivative **1** was identified as a selective thrombin inhibitor, equally active *in vitro* as dabigatran, but also endowed of additional selective inhibition of AChE. Based on a wider set of structurally related compounds, the molecular determinants responsible of the multiple activities towards different targets were rationally investigated by molecular cross-docking screens.

	K_i (μM)			
	fIIa	**fXa**	**AChE**	**BChE**
 **(1)**	0.0061	5.60	0.058	6.95
dabigatran	0.0042			
donepezil			0.021	2.25

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Identification and characterization of a potent TRPM8 antagonists with in vivo analgesic properties

Di Matteo F., [a] Musella S.,[a] Bertamino A.,[b] Ostacolo C.,[c] Medina A.,[d] Di Sarno V.,[b] Lauro G., [b] Ciaglia T., [b] Pepe G., [b] Basilicata M. G., [b] Cristiano C., [c] Gonzalez-Rodriguez S., [d] Fernandez-Carvajal A., [d] Bifulco G.,[b] Russo R.,[c] Gomez-Monterrey I.,[c] Campiglia P.[a,b]

[a] European Biomedical Research Institute (EBRIS); [b] Department of Pharmacy, [c] University of Salerno; Department of Pharmacy, University Federico II of Naples; [d]IDiBE, Universitas Miguel Hernández of Elche

TRPM8 (Transient receptor potential melastatin type 8) channel is a transmembrane Ca^{2+}−permeable nonselective cation channel activated by cold temperatures (10−28 °C) and different synthetic and natural molecules.[1] TRPM8 is involved in a wide range of physiological and pathological processes: in the last years has been observed that the TRPM8 overexpression in sensory neurons is related to neuropathic pain. For these reasons, the design of TRPM8 antagonists became an attractive strategy for neuropatic pain pharmacological treatments.[1,2]

Recentely, we have reported the synthesis and pharmacological evaluation of a small triptamine based library designed as TRPM8 ion channel modulators [3]. Two of the synthesized derivatives, (**12** and **21)**, were shown to be effective TRPM8 antagonist and agonist, respectively. [1,2] In order to rationalize the SAR of **12**, we previously built a model of TRPM8, based on the homology model by Taberner et al. [4]. In particular, we used a simplified version of the model and proposed that our antagonist docked at a putative binding site in the VSLD cavity. Subsequently, on the basis of crio-EM derived *ficedula albicollis* TRPM8 ($TRPM8_{FA}$) model, we generated a second hTRPM8 model, showing significant differences with respect to previously reported one. In particular, the location of several residues involved in modulator binding was redifined and this different arrangement was considered to design a new series of antagonists. Among these, the tryptophan derivative **14** was identified as a most potent (IC_{50} 0.2 ± 0.2 nM) and selective TRPM8 in-vitro antagonist. [5] However, in vivo experiments evidenced a metabolic instability for compound **14** causing its short lasting effect. Considering these results and following our interest in the TRPM8 modulation, in this study we present the design, synthesis, pharmacological characterization and metabolic stability evaluation of conformationally restricted analogues of compound **14** [6]. We decided to explore three different scaffolds based on thetrahydrobetacarboline nucleus as result of triptophane conformational restriction. This work allowed us to extend our knowledge about structural requirements needed to bind TRPM8. Moreover one of newly sintesized derivatives, compound **31a**, exibited a significative in vitro activity and a more permanent in vivo effect.

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Scaffold Hybridization Strategy in the Discovery of New Dopamine D_3 Receptor-Selective or Multitarget Ligands

Pegi Pavletić, Fabio Del Bello, Gianfabio Giorgioni, Wilma Quaglia, Alessandro Piergentili

School of Pharmacy, University of Camerino, 62032 Camerino (Italy)

Dopamine is a catecholamine neurotransmitter produced in several areas of the brain. It is involved in various physiological functions by interacting with specific receptors, members of the G protein-coupled receptor superfamily. They are classified in two main groups, namely D1-like, including D1 and D5 receptors (DRD1 and DRD5), and D2-like, comprising of D2, D3 and D4 receptors (DRD2, DRD3 and DRD4) [1]. DRD3 is a potential target for the treatment of several disorders, including Parkinson`s disease, substance use disorders, restless leg syndrome, schizophrenia and depression [2]. However, it exhibits high homology with the other dopaminergic subtypes, especially with DRD2, resulting in no therapeutically approved selective DRD3 drug [2]. A promising strategy for improving DRD3 selectivity consists of the development of bitopic ligands bearing an aryl piperazine as the primary pharmacophore (PP) linked by a proper alkyl chain to an arylcarboxamide as the secondary pharmacophore (SP) [3]. We have recently demonstrated that the 1,4-dioxane nucleus represents a bioversatile carrier of ligands interacting with different receptor systems, including D2-like receptors [4]. In particular, two properly substituted 1,4-dioxane compounds endowed with fruitful multitarget combinations have been identified as new pharmacological tools potentially useful for the treatment of Parkinson's disease and schizophrenia [4].
Based on these observations, with the aim of analyzing the role of the properly substituted 1,4-dioxane scaffold as an SP of bitopic compounds targeting DRD3, hybrid ligands bearing the *N*-(2,3-dichlorophenyl)piperazine nucleus as the PP linked by an unsubstituted or properly substituted butyl chain to the aryl-1,4-dioxane-2-carboxamide scaffold as the SP (Figure 1), have been prepared and studied.

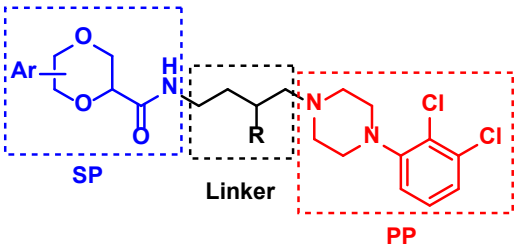

Figure 1. *Structures of D3DR bitopic ligands bearing an aryl-1,4-dioxane-2-carboxamide scaffold.*

All the compounds were tested by radioligand competition binding assays at DRD2, DRD3 and DRD4 expressed in HEK293 cells. Moreover, the biological profiles of the most promising compounds were further evaluated in binding assays at other selected targets (DRD1, 5-HT1AR, 5-HT2AR, 5-HT2CR) and in functional assays at receptors for which they have shown the highest affinities. New D3-selective or multitarget agents potentially useful for the treatment of central nervous system disorders have been identified, and their biological profiles are discussed.

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Medicinal chemistry approach towards sustainable drugs for neurodegeneration

*Michele Rossi,[a] Alessandra Salerno,[a] Andressa Souza de Oliveira,[b] Thais de Araujo Marques Ferreira,[b] Nicola Rizzardi[a] Christian Bergamini,[a] Carlos Alberto Manssour Fraga,[c] Christophe Blanquart,[d] Philippe Bertrand,[e] Luiz Antonio Soares Romeiro,[b] Maria Laura Bolognesi [a]**

[a]*Alma Mater Studiorum - University of Bologna, Dept. Pharmacy and Biotechnology, Bologna, 40126, Italy;* [b]*Department of Pharmacy, Health Sciences Faculty, University of Brasília, Campus Universitário Darcy Ribeiro, Brasília, DF, Brazil;* [c]*Laboratory of Synthesis and Evaluation of Bioactive (LASSBio), Institute of Biomedical Sciences, Federal University of Rio de Janeiro, Rio de Janeiro 21941-901, Brazil;*[d]*CRCINA, INSERM, Université de Nantes, 44007 Nantes, France;* [e]*Institut de Chimie des Milieux et Matériaux de Poitiers, UMR CNRS 7285, 4 rue Michel Brunet, TSA 51106, B27, F-86073 Poitiers Cedex 09, France; Réseau Epigénétique du Cancéropôle Grand Ouest, France.*

Alzheimer's disease (AD) represents a global epidemic that affects 35 million people worldwide: already 60% of AD patients live in low- and middle-income countries and this will rise to 71% by 2050. Several efforts have been done to address the complex AD etiology and there is a great impetus to identify alternative targets. Among others, restoring the perturbed acetylation homeostasis of the neurodegenerative state by histone deacetylase (HDAC) inhibitors, as well targeting metal dyshomeostasis, have been considered emerging hypotheses holding great promise.

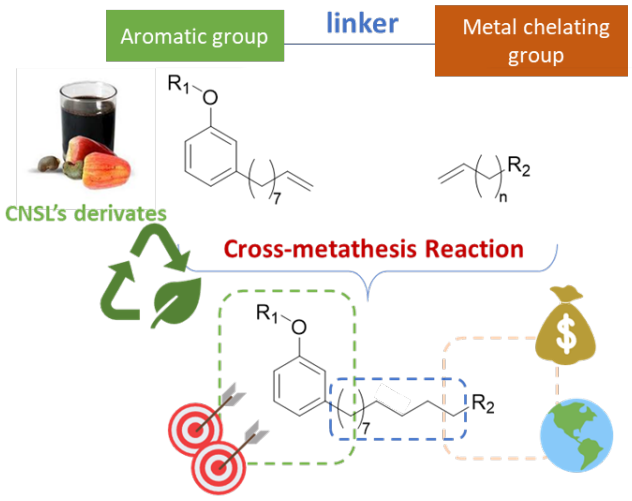

Figure 1: Sustainable Drug Design

The development of effective, sustainable, and accessible drugs for AD has therefore attracted much attention lately. Consistently with our previous works,[1,2] we aimed to explore the potential of cashew nut-shell liquid (CNSL) for the sustainable production of drugs potentially endowed with anti-neurodegenerative activity. CNSL is a byproduct of the cashew industry, interesting in terms of waste valorization for the production of new chemicals and because its main components (anacardic acid, cardol and cardanol) presents innate multi-factorial activities, *i.e.* anti-inflammatory, analgesic and HDAC inhibition. We have recently reported HDAC inhibitors derived from CNSL showing a promising profile. Although effective, the semisynthetic route involving the use of Jones Reagent, is clearly not compatible with sustainability criteria. Thus, to overcome this challenge we looked for greener synthetic strategies (Figure 1). Cross-metathesis is an innovative, convenient, and sustainable reaction for such purpose. Thanks to the protocol versatility we have been able to design and synthetized new compounds with aliphatic linker bearing different aromatic group derived from cardanol and combine it with various metal-binding groups. Assays to characterize the biological profile of such compounds are currently ongoing. Overall, we developed a sustainable and versatile synthetic protocol to harness CNSL's derivatives to potentially obtain a broad library of compounds.

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Structure-Based Virtual Screening for the identification of new Selenoproteins Inhibitors for Cancer Therapy

Giuseppe Lamanna[a,b], Pietro Delre[a,b], Filippo Prencipe[b], Filomena Rossi[c], Diego Tesauro[c], Luisa Ronga[d], Ryszard Lobinski[d], Giuseppe Felice Mangiatordi[b] and Michele Saviano[b]

[a]*Dipartimento di Chimica, Università Degli Studi di Bari "Aldo Moro", Bari, Italy;* [b]*Consiglio Nazionale Delle Ricerche, Istituto di Cristallografia, Bari, Italy;* [c]*Department of Pharmacy and Interuniversity Research Centre on Bioactive Peptides (CIRPeB), University of Naples "Federico II;* [d]*Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Pau, France*

Selenoproteins (SPs), *i.e.*, proteins containing selenocysteine as the 21st "naturally occurring" amino acid, are today emerging as promising pharmaceutical targets in the field of oncology. As reported in the literature,[1] SPs activity is closely linked to carcinogenesis. Among the 25 different SPs identified so far, thioredoxin reductase (TrxR) and glutathione peroxidase (GPx) have attracted significant attention in the last few years as attractive targets, being overexpressed in most tumors.[2-3] Although several small molecules (SMs) were recently proved to inhibit TrxR,[4-6] the information regarding the protein portion responsible for the SMs recognition is still limited due to the absence, in the Protein Data Bank (PDB), of TrxR structures bound to inhibitors. Building on this evidence, we performed an extensive analysis of the X-ray crystallographic structures retrieved from the PDB and identified a TrxR druggable cavity, likely responsible for the interaction with the known inhibitors using *SiteMap*, available from the Schrodinger suite 2020-1. The entire TrxR was scanned to localize binding sites whose size, functionality, and extent of solvent exposure meet specifications typical of pockets of interest for structure-based investigations. *SiteMap* enables us to assess the site propensity for ligand binding with a high degree of confidence and even to predict its druggability. The identified pocket was then employed to set up a technological platform to undertake docking virtual high-throughput screening. In particular, the whole *Asinex Elite* dataset, comprising 87,107 compounds devoid of potential ADMET problems, was screened and the obtained results were analyzed by combining conventional docking scores and MMGBSA binding free energies. The study allowed us to propose several candidates as new non-covalent TrxR inhibitors to be experimentally tested through *in-vitro* assays.

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Therapeutic potential of TRPM8 antagonists in prostate cancer

Veronica Di Sarno[a], Marzia Di Donato[b], Carmine Ostacolo[c], Pia Giovannelli[b], Isabel M. Gomez Monterrey[c], Pietro Campiglia[a], Antimo Migliacci[b], Alessia Bertamina[1] and Gabriella Castoria[b]

[a]Department of Pharmacy, University of Salerno, Via G.Paolo II, 84084, Fisciano (SA); [b]Department of Precision Medicine, School of Medicine- University of Campania 'L. Vanvitelli', Via L. De Crecchio 7, 80138 Naples; [c]Department of Pharmacy, University Federico II of Naples, Via D. Montesano 49, 80131, Naples

Transient receptor potential melastatin-8 (TRPM8) is a hugely distributed non-selective calcium permeable ion channel [1] and it is involved in many pathological processes, such as pain [2], migraine [3] and overactive as well as painful bladder syndromes. TRPM8 channel is directly involved in calcium homeostasis and is regulated by androgens [4], estrogens [3], and growth factors. [5] As such, it represents a very promising target in solid cancers including Prostate Cancer (PC).[6] We here investigated the effects of TRPM8 modulators in PC proliferation, motility, and invasiveness. Patch-clamp and calcium fluorometric assays were used to characterize the synthesized compounds. Androgen stimulated PC-derived LNCaP cells were challenged with the compounds and the DNA synthesis was investigated for preliminary screening. The most effective compounds were employed to inhibit the migration and invasiveness of LNCaP cells. The molecular targets were identified using transcriptional and non-transcriptional reporter assays. Co-immunoprecipitation analysis revealed the interference of selected compounds in the androgen-induced Androgen Receptor (AR)/TRPM8 complex assembly. TRPM8 antagonists inhibit the androgen-dependent LNCaP cell proliferation, migration and invasiveness. No effects were recorded in various androgen-insensitive PC cells. The selected antagonists interfere in non-genomic androgen actions and abolish the androgen-induced AR/TRPM8 complex assembly as well as the increase in intracellular calcium levels in LNCaP cells. Our results shed light in the processes controlling PC progression and make TRPM8 as a 'druggable' target in the androgen receptor-expressing PC.

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Targeting the allosteric sites of the B-Raf protein kinase through an *in silico* approach

Luca Pinzi[a], *Giulio Rastelli*[a]

[a] *Department of Life Sciences, University of Modena and Reggio Emilia, Via Giuseppe Campi 103, 41125 Modena, Italy.*

B-Raf is a Serine/Threonine kinase involved in the regulation of the MAPK/ERK signaling pathway. Research findings demonstrated that B-Raf is one among the most frequently deregulated protein kinases in human cancers, especially when driven by oncogenic point mutations, the V600E being the most common. Although several anticancer drugs targeting *wt* and mutant B-Raf proteins have been marketed so far, ATP-competitive inhibitors of this protein present several drug resistance and side effects issues, which often limit their therapeutic utility. Notably, recent studies demonstrated that targeting the type III allosteric site of kinases (*e.g.*, the CDK2 and EGFR) is feasible with drug-like compounds, and that B-Raf possesses an allosteric pocket similar to that of the oncogenic $EGFR^{T790M}$ protein [1-3]. Moreover, very recently peptidomimetic inhibitors of Raf dimerization have also been reported, demonstrating that blockage of this kinase through such a mechanism represents a valuable approach to overcome drug resistance to currently available ATP-competitive inhibitors [4]. To identify the structural determinants conferring binding affinity to the B-Raf allosteric pockets, a series of *in silico* analyses on publicly available chemical, biological and structural data was performed. In particular, chemoinformatic analyses on a set of known ligands and molecular dynamics simulations on selected crystallographic complexes allowed to identify favorable anchoring points on B-Raf allosteric pockets and structural determinants potentially important for the design of compounds able to exert B-Raf inhibitory activity. Finally, virtual screening campaigns integrating different ligand- and structure-based *in silico* approaches were performed to identify compounds able to inhibit this protein with allosteric mechanisms.

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Structure-Guided Fragment-Based Approach to Identify New Heme Oxygenase-1 Inhibitors

Giuseppe Floresta [a], Antonino N. Fallica [b], Loredana Salerno [b], Valeria Sorrenti [b], Sebastiano Intagliata [b], Antonio Rescifina [b], Valeria Pittalà [b]

[a] Department of Analytical, Environmental and Forensic Sciences, King's College London, London – UK; [b] Department of Drug and Health Sciences, University of Catania, Catania – IT Affiliation

Up-regulation of heme oxygenase-1 (HO-1) has been often detected in different human malignancies [1,2]. Since poor clinical outcomes are reported in these cases, HO-1 inhibition is recognized as new anticancer approach [3,4]. With the aim of identifying novel HO-1 inhibitors, we performed a structure-guided fragment-based approach to identify new lead compounds. Different portions of the selected molecules were analyzed, and the newly designed series of compounds were virtually evaluated. The growing experiments of the classical HO-1 inhibitors structure led us to the identification of different hit-compounds. Chemical synthesis of six selected molecules was set up and compounds have been synthesized in high yield. Biological activity data showed for compounds **1** and **2** a HO-1 inhibition activity (IC_{50}) of 1.01 and 0.90 µM, respectively. This study suggested that our growing approach was successful, and these results are ongoing for further development.

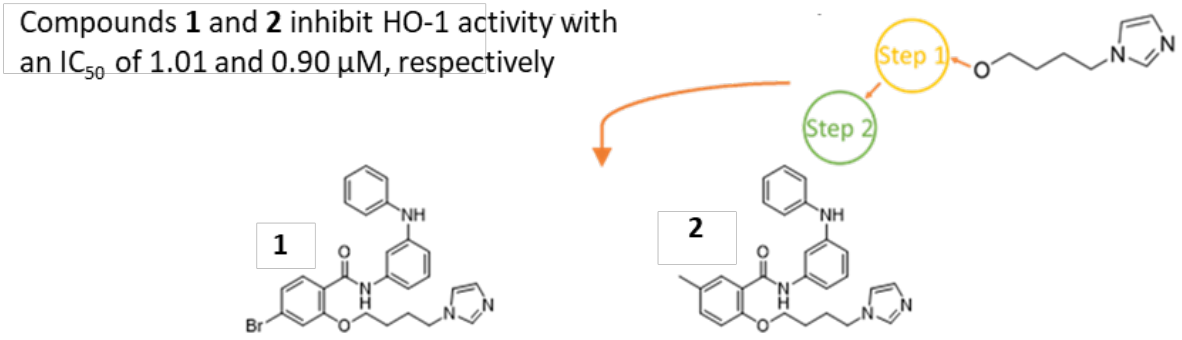

Figure 1. Structure-guided fragment-based approach to identify new HO-1 inhibitors

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A New Potential Target in Oncological Therapy: The Interaction Between Gab2 With SH3-Domain of Gbr2

Michela Puxeddu;[a,*] *Antonio Coluccia;*[a] *Giuseppe La Regina;*[a], *Stefano Gianni;*[b] *Romano Silvestri*[a]

[a]*Laboratory affiliated to Istituto Pasteur Italia — Fondazione Cenci Bolognetti, Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza Università di Roma, Piazzale Aldo Moro 5, 00185, Rome, Italy;* [b]*Istituto Pasteur — Fondazione Cenci Bolognetti, Dipartimento di Scienze Biochimiche "A. Rossi Fanelli" and Istituto di Biologia e Patologia Molecolari del CNR, Sapienza Università di Roma, 00185, Rome, Italy.* **michela.puxeddu@uniroma1.it.*

Gab2 is a scaffolding protein that plays a key role in cellular proliferation, migration ad differentiation. Indeed, it is overexpressed in many types of cancer's tissues as breast gastric, lung, and colorectal. The interaction between Gab2 and the *C*-terminal SH3 domain of Gbr2 represents one of the first steps of activation of the Ras/Erk, an important proliferation-signalling pathway, thus being a valuable potential anticancer drug target. Therefore, a virtual screening study allowed us to identify seven potential inhibitor molecules, which were tested through kinetic and equilibrium binding experiments. From the results obtained, the only compound that showed inhibitory activity against the above interaction is AN-465-J137-985 (Chart 1).[1] Molecular docking studies on Gbr's SH3-domain of this derivative provided insights into the molecular determinants responsible for its high affinity toward the target. The superimposition of the AN-465-J137-985 proposed binding and Gab2 core highlighted that three aromatic rings were superimposable with Pro512 and Val513 side chains, besides the Arg515 backbone is similar to hydrophobic contact observed for the substrate (Figure 1). To further investigate the effect of AN-465-J137-985 we treated A549 and H1299, lung cancer cell lines, with increasing doses of AN-465-J137-985, evaluating the potential anti-cancer effects of this molecule. The compound was shown to significantly inhibit the growth of both cancer cell lines. In particular, it exhibits values of lethal dose 50 (LD_{50}) of about 5 and 7 μM for H1299 and A549 cell lines, respectively.

Chart 1. Chemical structure of AN-465-J137-985.

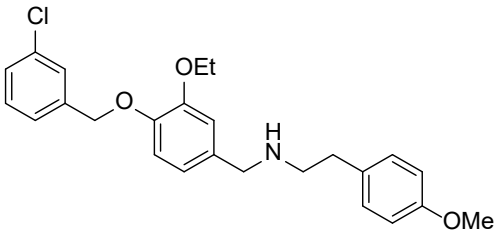
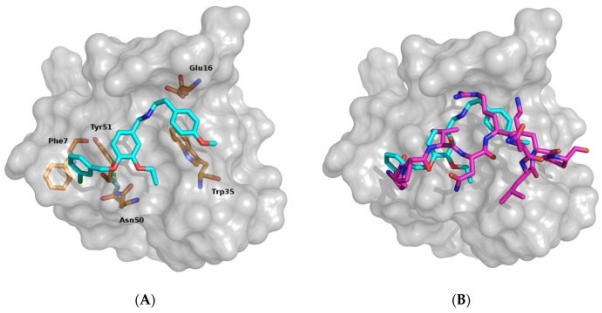


Figure 1. (**A**) Binding mode for derivative AN-465-J137-985. (**B**) Superimposition of AN-465-J137-985 proposed binding and Gab2a core binding.



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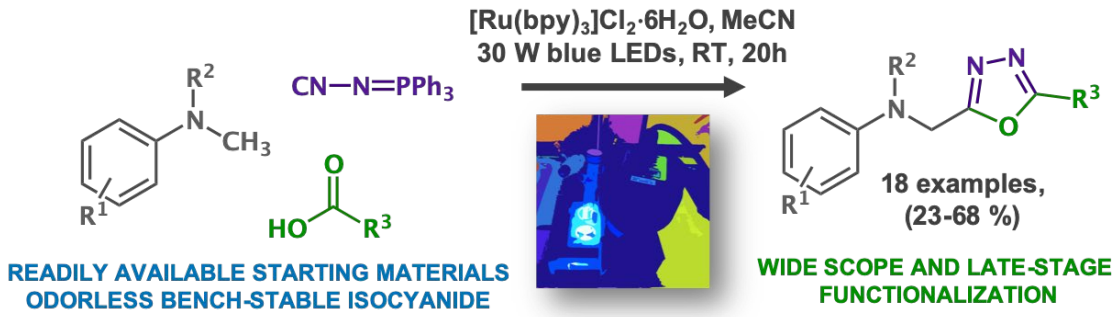
Visible-Light Photocatalytic Ugi/Aza-Wittig Cascade Towards 2-aminomethyl-1,3,4-oxadiazole derivatives

Camilla Russo[a], Rolando Cannalire[a], Francesca Brunelli[b], Gian Cesare Tron[b], Mariateresa Giustiniano[a]*

[a] *Department of Pharmacy, University of Naples Federico II, via D. Montesano 49, 80131, Napoli, Italy;*
[b] *Department of Drug Science, University of Piemonte Orientale, Largo Donegani 2, 28100, Novara, Italy*

Considering the *status* of privileged scaffold in medicinal chemistry deserved by the oxadiazole core, a new visible light photocatalytic multicomponent reaction (MCR) involving *N*-alkyl-*N*-methylanilines, *N*-isocyanoiminotriphenyl phosphorane, and carboxylic acids leading to 1,3,4-oxadiazole derivatives was developed[1]. This new synthetic approach allowed to expand to aromatic amines the substrate scope of previously reported strategies, which were all limited to strongly nucleophilic secondary aliphatic amines[2], [3], [4]. The use of photoredox catalysis was key to promote the *in situ* oxidation of *N*-alkyl-*N*-methylanilines to the corresponding iminium ions[5], thus leading to a radical/polar crossover towards an Ugi-like/*aza*-Wittig domino sequence. The mild reaction conditions enabled a broad substrate scope and a good functional group tolerance, as further highlighted in the late stage functionalization of amino acids and drugs. Additionally, a 2-step one-pot protocol involving the photocatalytic MCR followed by acid hydrolysis of the 1,3,4-oxadiazole derivatives was developed as an expeditious and green synthetic approach for the obtainment of pharmaceutically relevant asymmetric diacylhydrazines.



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Ciprofloxacin and Norfloxacin Nitric Oxide Photo-donor Hybrids: From Antibacterial to Anticancer Agents

Antonino N Fallica [a], *Carla Barbaraci* [a], *Maria Tindara Ignazzitto* [a], *Elisabetta Tomarchio* [a], *Davide Gentile* [a], *Emanuele Amata* [a], *Marzia Bruna Gariboldi* [b], *Viviana Teresa Orlandi* [b], *Antonio Rescifina* [a], *Greta Varchi* [c], *Agostino Marrazzo* [a]

[a] *Department of Drug and Health Sciences, University of Catania, V.le Andrea Doria 6, 95125, Catania, Italy;*
[b] *Department of Biotechnology and Life Sciences, University of Insubria, Via JH Dunant 3, 21100, Varese, Italy;*
[c] *Institute for the Organic Synthesis and Photoreactivity, Via Piero Gobetti, 101, 40129, Bologna, Italy.*

Fluoroquinolones represent a class antimicrobial agents prescribed for the treatment of urinary and respiratory infections. Structure-activity relationships for this class of compounds highlighted the structural features responsible for an optimal antimicrobial activity. Interestingly, insertion of substituents on the amine function incorporated in the heterocyclic ring at the 7-position can abolish the antimicrobial properties of these compounds in favor of anticancer effects [1]. Nitric oxide (NO) is a short-lived gasotransmitter involved in the control of several physiological conditions. It has been widely demonstrated that micromolar concentrations of NO can promote cytotoxicity and cell death [2]. Because of its short half-life, the direct administration is challenging. Therefore, several NO donors have been investigated with NO photo-donors representing one of the best tools exploitable for a spatiotemporally release of NO directly at the site of interest. With this in mind, we designed and synthesized twelve Ciprofloxacin and Norfloxacin derivatives in which the fluoroquinolone nucleus has been linked to a 4-nitro-3-trifluoromethylaniline moiety responsible for the light-triggered release of NO. Almost all compounds displayed strong antiproliferative activity on a small panel of cancer cell line, with encouraging results obtained in the MDA-MB-231 triple negative breast cancer cell line and the MCF7/ADR breast cancer cell line. On the other hand, the novel derivative have lost any antimicrobic effects in *Pseudomonas aeruginosa* PAO1 bacterial strain.

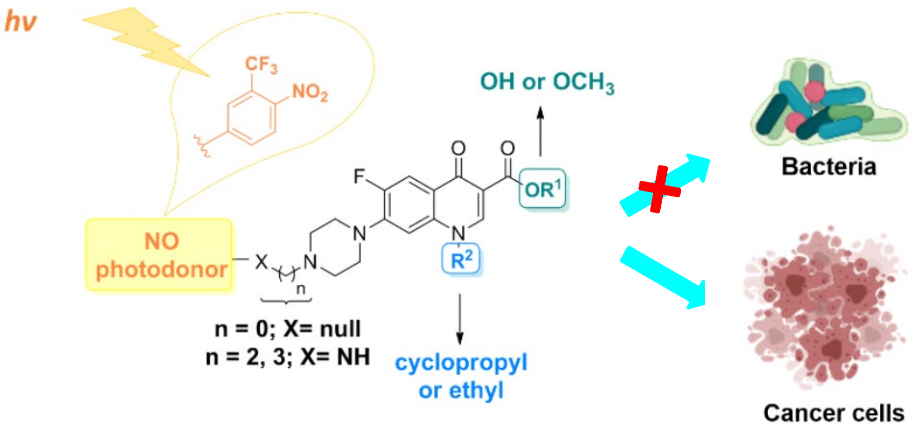

Figure 1. General Structure of Fluoroquinolone Nitric Oxide Photo-donor Hybrids

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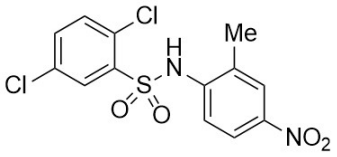
Novel Sulfonamide Inhibitors of β-Catenin Signaling As Anticancer Agents

Sebastiani, J.;[a,*] Coluccia, A.;[a] La Regina, G.;[a] Canettieri, G.;[b] Silvestri, R.[a]

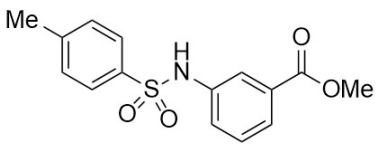
[a]*Laboratory affiliated to Istituto Pasteur Italia – Fondazione Cenci Bolognetti, Dipartimento di Chimica e Tecnologie del Farmaco, Sapienza Università di Roma, Piazzale Aldo Moro 5, 00185, Rome, Italy.* [b]*Laboratory affiliated to Istituto Pasteur Italia – Fondazione Cenci Bolognetti, Dipartimento di Medicina Molecolare, Sapienza Università di Roma, Viale Regina Elena 291, 00161, Rome, Italy.* **sebastiani.jessica@uniroma1.it.*

The Wnt/β-catenin pathway is often found deregulated in cancer. β-catenin is a multifunctional protein with a central role in physiological homeostasis. Its aberrant high expression, regulated by the presence of the Wnt ligand, leads to various diseases including cancer. It acts as both transcriptional co-regulator and an adaptor protein for intracellular adhesion. In more than half of all cancer cases, such as colorectal carcinoma, breast cancer, liver carcinoma, melanoma and leukemia, β-catenin accumulates within the nucleus or cytoplasm. Specific drugs against this signaling pathway for clinical treatments have not been approved yet. Herein we report compounds with *N*-Aryl benzenesulfonamide scaffold, able to interfere with the β-catenin signaling.[1] Previous studies on sulfonamides have highlighted some inconsistencies in terms of structure-activity relationship studies, therefore we decided to further explore this class of Wnt/β-catenin inhibitors. Starting from the most active derivatives previously reported FH535 (**1**) and MSAB (**2**), we synthesized a small test set of compounds (3-13), by changing the substituent at ring A and the position of the ester functional group at the ring B (Chart 1). All new sulfonamides were tested as inhibitors of Wnt/ β-catenin pathway and showed IC_{50} values ranging from 7.0 to 18.3 μM. In the luciferase-based TOPFlash assay four analogs were more effective than MSAB, used as reference compound. Derivatives with the methoxy, chlorine or trifluoromethyl at position 4 and the ethyl ester at position 4' showed the highest inhibition of β-catenin pathway. With the exception of one derivative, the presence of a methoxy or a nitro group had a detrimental effect on the inhibition of β-catenin. These data suggest that both the substituent and the nature and position of the group at the ring B play key roles in the inhibition of β-catenin. In particular, two compounds has also been tested for the capability to inhibit colon cancer cell growth by affecting β-catenin and c-MYC expression levels.

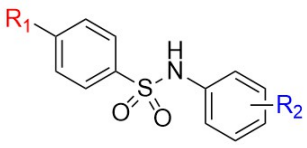
Chart 1. Chemical structures of compounds **1-3**.



1 (FH535)



2 (MSAB)



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Two mixed valence diruthenium (II,III) isomeric complexes show different anticancer properties

Elisabetta Barresi,[a] Iogann Tolbatov,[b] Tiziano Marzo,[a] Elisa Zappelli,[a] Alessandro Marrone,[c] Nazzareno Re,[c] Alessandro Pratesi,[d] Claudia Martini,[a] Sabrina Taliani[a] Federico Da Settimo,[a] and Diego La Mendola[a]

[a]Department of Pharmacy, University of Pisa, Via Bonanno Pisano, 6, 56126, Pisa, Italy; [b]Institut de Chimie Moleculaire de l'Université de Bourgogne (ICMUB), Université de Bourgogne Franche-Comté (UBFC), avenue Alain Savary 9, Dijon, France; [c]Department of Pharmacy, University of "G. D'Annunzio" Chieti-Pescara, Via dei Vestini, I-66100 Chieti, Italy; [d]Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi, 13, 56124 Pisa, Italy.

Platinum-based agents, including cisplatin, carboplatin and oxaliplatin are some of the most commonly used chemotherapy drugs [1]. Behind their effectiveness, their use is limited by drug resistance and side effects [2], thus huge efforts are devoted to the design of improved antineoplastic agents. Among the several effective strategies developed [3], the use of paddlewheel ruthenium-based complexes characterized by the presence of a direct metal-metal bond and a (II,III) mixed valence is very interesting [4].

We recently synthesized the Ru_2(II,III) compound $[Ru_2(EB106)_4Cl]$ where EB106 is an indolylglyoxylyl dipeptide endowed with anticancer activity against glioblastoma multiforme (GBM) cells (**Fig. 1**) [5,6]. However, $[Ru_2(EB106)_4Cl]$ -at variance with EB106- was completely inactive in GBM models, as a consequence of its high stability that in turn is due to the nature of the ligand. Also, the steric protection operated by the indolylglyoxylyl moiety prevents the attack of the water molecules or other potential ligands at the Ru metal centers. To deepen our studies on these systems, we developed the complex $[Ru_2(EB776)_4Cl]$ (**Fig. 1**), characterized by the presence of EB776 (isomer of EB106) that coordinates the Ru_2 core. This complex should be more reactive, and thus more active as anticancer agent, because of the increased accessibility of the Ru_2 core to the attacking nucleophiles, compared to $[Ru_2(EB106)_4Cl]$.

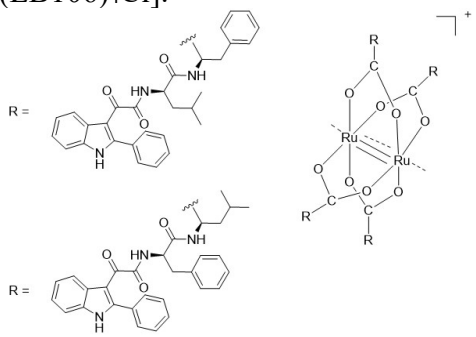

Fig. 1. Structures of EB106 (top left) and EB776 (bottom left) and general structure of the paddle-wheel Ru2(II,III) complexes (right).

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Novel GABARAP inhibitors: design, synthesis, and preliminary biological evaluation of asymmetric N-C type 1,1-bis-triazole derivatives as potential anticancer agents

Stefania Villa [a], Matteo Mori [a], Eleonora Fratus [a], Samuele Ciceri [a], Enrico Mario Alessandro Fassi [a], Jacopo Sgrignani [b], Mariangela Garofalo [c] and Giovanni Grazioso [a]

[a] Dipartimento di Scienze Farmaceutiche, Università degli Studi di Milano, via L. Mangiagalli 25, 20133 Milano, Italy; [b] Istituto di Ricerca in Biomedicina (IRB), Università della Svizzera Italiana (USI), Via V. Vela 6, CH-6500, Bellinzona, Svizzera; [c] Dipartimento di Scienze Farmaceutiche e Farmacologiche, Università di Padova, via F. Marzolo 5, 35131 Padova - Italy

Standard cancer treatments may be combined with new therapeutic strategies to increase efficacy and to overcome resistance problems, fighting the tumor through synergic mechanisms. Autophagy has been shown to have a pro-survival role in most advanced cancers, by promoting tumor progression, facilitating tumor adaptation to different stress conditions, and reducing the efficacy of drug treatments. In this regard, autophagy inhibition has recently emerged as a promising anticancer strategy. [1] Therefore, an innovative approach may consist in the discovery of new potent and specific inhibitors of mAtg proteins that could play a pivotal role in the autophagy process. For this reason, the aim of this research is the design and synthesis of potential inhibitors of GABARAP, a member of the mAtg8 family involved in autophagosome closure and autophagosome-lysosome fusion. Since the proteins involved in the autophagy process are conserved across most eukaryotic phyla, it has been suggested that compounds synthesized against *Pf*Atg8 could inhibit mAtg8 proteins too. This hypothesis was supported by the structural alignment of *Pf*Atg8 and GABARAP, which revealed a similar fold. New molecules were designed by a target-based computational approach, improving the strength of the interactions between the starting compounds and the available residues in the binding site of GABARAP. *In silico* studies, including docking calculations, MD simulations, cluster analyses, and MM-GBSA calculations, led to the design of an asymmetric N-C-type 1,1-bis-triazole derivative as a potential GABARAP inhibitors, the most promising compound was synthetized and biologically evaluated by SPR and MST assays.

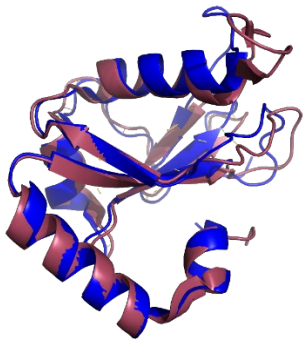

Figure 1. *Structural alignment of PfAtg8 (PDB: 4EOY) and GABARAP (PDB: 5YIR). PfAtg8 is raspberry and GABARAP is blue.*

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[2]

Identification of novel pyrazole derivatives as inhibitors of lysine acetyltransferase p300

Viviano, M.;[a] *Milite, C.*;[a] *Feoli, A.*;[a] *Lauro, G.*;[a] *Li, H.*;[b] *Bifulco, G.*;[a] *Castellano, S.*;[a] *and Sbardella, G.*[a]

[a] *Dipartimento di Farmacia, Università degli Studi di Salerno, Via G. Paolo II 132, 84084 Fisciano (SA), Italy;*
[b] *Tsinghua University, Center for Structural Biology, Beijing 100084, P.R. China*

Lysine acetylation is far from being fully understood, even after 50 years from its discovery [1]. Lysine acetyltransferases (KATs) are responsible of this chemical modification, that neutralizes the positive charge of lysine side chains, weakening the interactions between histones and DNA and, as a result, making chromosomal DNA more accessible [2]. Among the nuclear KATs, the acetyltransferase p300 (KAT3B) plays key roles in different cellular processes, implying that the dysregulation of its activity leads to many human diseases, including cancer [3, 4]. These observations suggest that p300 might represents a potential anticancer therapeutic target.
Starting from an Inverse Virtual Screening study, we recently identified the Cannabinoid Receptor 1 (CB1) inverse agonist Rimonabant as a new potential p300 inhibitor and confirmed this outcome in in cell and in vivo studies [5]. Therefore, with the aim to identify new p300 modulators, a computational model was developed, and a first series of pyrazole derivatives synthesized. Prompted by our interest in the discovery of small molecule modulators of epigenetic targets, after further structural optimization (Figure 1) here we report the identification of a new series of p300 inhibitors, that might represent new opportunities to investigate the role of this protein in chromatin biology and drug discovery.

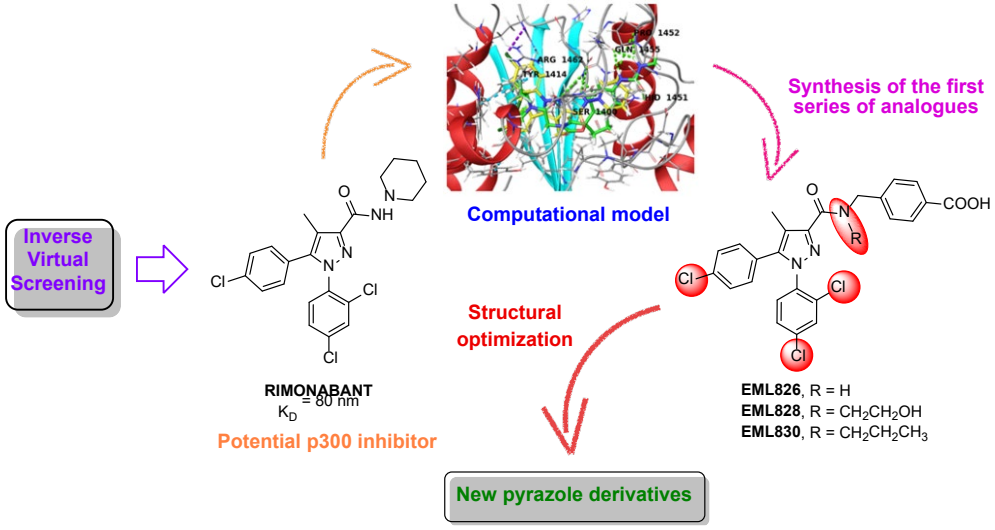

Figure 1.

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Dual-ligands Sigma/HDACi: a multitarget approach as potential strategy for anticancer therapy

Carla Barbaraci,[a,b] Viviana di Giacomo,[c] Claudia Giovanna Leotta,[b] Maria Dichiara,[a] Vincenzo Patamia,[a] Annalisa Maruca,[d,e] Emanuele Amata,[a] Antonio Rescifina,[a] Stefano Alcaro,[d,e] Giovanni Mario Pitari,[b] Ivana Cacciatore,[c] Agostino Marrazzo[a]

[a]*Department of Drug and Health Sciences, University of Catania, Viale A. Doria 6, 95125 Catania, Italy*
[b]*Vera Salus Ricerca S.r.l, Via Sigmund Freud 62/B, 96100 Siracusa, Italy*
[c]*Department of Pharmacy, University "G. d'Annunzio" Chieti-Pescara, Via dei Vestini 31, 66100 Chieti, Italy.*
[d]*Department of Health Sciences, University of "Magna Græcia" Catanzaro, Viale Europa, 88100 Catanzaro, Italy*
[e]*Net4Science academic spinoff, Università "Magna Græcia" di Catanzaro, Viale Europa, 88100 Catanzaro, Italy*

The drug discovery paradigm “one-molecule, one-target” remains a major breakthrough in the scientific world. On the other hand, polypharmacology is emerging as a new paradigm to develop small molecules for the treatment of multifactorial diseases such as cancer, being able to modulate multiple targets simultaneously [1]. Multi-ligands drugs present the advantage of reducing drug resistance, but also drug-drug interactions, therapeutic doses and therefore side effects, simplifying the pharmacokinetic profiles [2]. Growing interest in Sigma receptor (σR) ligands and the encouraging developments of histone deacetylase inhibitors (HDACi) in the field of cancer therapy suggest that they may represent ideal targets for the application of this approach [3]. On these grounds, appropriate functional groups were selected, providing together a single pharmacophore allowed to fit into the pharmacophoric model of both σR or HDAC enzyme [4].

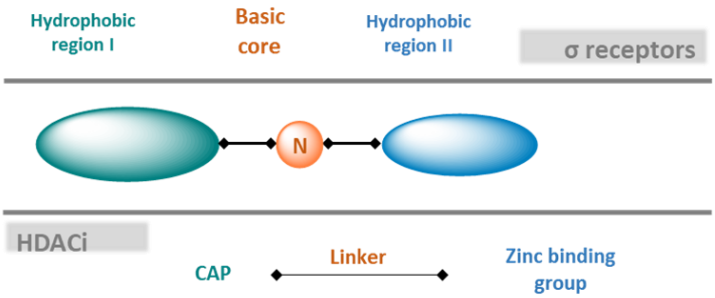

Figure 1. Design of Sigma/HDAC hybrids, merging the pharmacophoric models of σR ligands and HDACi

In this way, the new synthesized “dual-ligands” should interact as such on the molecular targets considered, antagonizing the σ_1R and inhibiting HDAC enzyme. In order to confirm this hypothesis, molecular modelling studies were carried out to investigate the interactions of the novel chemical entities with the considered targets. Biological screening on several cancer cell lines was realized to determine their anticancer activity. Results show that some of the novel compounds reduced cell proliferation in different cancer cells, identifying multiple opportunities for their employment as potential anticancer agents.

The project is supported by a MUR PRIN project (code 201744BN5T).

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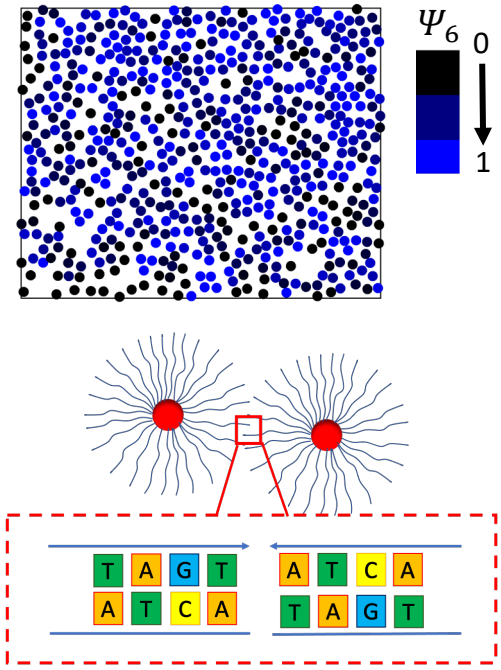
CHIMICA FISICA (FIS)

- Orals
- Posters

Blunt-end driven assembly of star-like dsDNA coated colloids

I. Romero-Sanchez,[a,b] I. Pihlajamaa,[c] N. Adzic,[c] L. E. Castellano-Torres,[b] E. Stiakakis,[d] C. N. Likos,[c] M. Laurati[a]

[a] Dipartimento di Chimica & CSGI, Università di Firenze, 50019 Sesto Fiorentino, Italy, [b] División de Ciencias e Ingenierías, Universidad de Guanajuato, 37150 León, Mexico, [c] Faculty of Physics, University of Vienna, Bolzmanngasse 5, A-1090 Vienna, Austria, [d] Forschungszentrum Jülich, Institute of Complex Systems 3, Leo-Brandt-Strasse, 52425 Jülich,Germany



We investigated assembly phenomena driven by base-stacking interactions between blunt-ends of long double-stranded (ds) DNA grafted onto the surface of polystyrene beads. In the osmotic regime of the dsDNA brushes, particle tracking experiments on increasingly dense suspensions reveal progressive shrinking of the brushes and complex aggregation with a non-monotonic variation of the degree of ordering and the dynamics of the system. The figure shows an exemplary rendering of a sample evidencing aggregation: the color scale indicates the value of the six-fold order parameter.
A detailed theoretical description of the forces acting on a single spherical brush and in a system of many brushes shows that monotonic shrinking is induced by the pressure exerted on a brush by the non-condensed counterions absorbed in neighbor brushes. With the help of MD simulations, we show that the non-monotonic shrinking and the complex aggregation phenomena observed experimentally can be reproduced when a short-range attractive interaction competes with the mid-range repulsive electrostatic interactions. Short-range attractions are attributed to blunt-end base-stacking interactions of dsDNA strands of neighboring brushes (sketched in the figure), which become relevant for stretched dsDNA configurations and small inter-digitation, conditions observed in the osmotic regime and for the crowded conditions of the experiments. To corroborate our interpretation, we show that the attractive interaction is strongly reduced and disappears with addition of increasingly large amounts of monovalent salt or with a progressive reduction of the grafting density of the particles. This result shows in addition that equilibrium and out-of-equilibrium colloidal assembly driven by base stacking, which does not require a detailed programming of strand sequences as for the more common base-pairing, is highly specific and can be finely tuned acting on easily controlled experimental parameters, such as salt concentration and temperature.

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Spectroscopic markers of heart failure: a Raman and FTIR study

Niki Tombolesi [a], Leonardo Pioppi [a], Raffaele Altara [b,c,d], Gustavo J.J. da Silva [b,c], Assunta Morresi [1], Marco Paolantoni [1], George W. Booz [d,e], Alessandro Cataliotti [b,c], and Paola Sassi [a]

[a]Department of Chemistry, Biology and Biotechnology, University of Perugia, Perugia, Italy;
[b]Institute for Experimental Medical Research, Oslo University Hospital and University of Oslo;
[c]KG Jebsen Center for Cardiac Research, University of Oslo, Oslo, Norway;
[d]Department of Pathology, or [e]Department of Pharmacology and Toxicology, School of Medicine, University of Mississippi Medical Center, Jackson, MS, USA

Heart failure (HF) is a major clinical challenge that is associated with a markedly increased risk of death [1]. It affects over 26 million people worldwide, accounts for the majority of hospitalizations among the elderly, and its prevalence continue to rise. Approximately half the patients with HF have normal contractility. This medical condition of HF with preserved ejection fraction (HFpEF) is characterized by cardiac hypertrophy and increased stiffness of the heart, which compromise ventricular relaxation and reduce stroke volume. Although the mechanisms responsible for the development of HFpEF are not fully understood, it is well known that nearly 80% of the patients with HFpEF have concomitant hypertension.

Here, we investigated whether early cardiac biochemical alterations can be detected during the progression of cardiac hypertrophy to HFpEF in a rat model of salt-induced hypertension. Fourier-transformed infrared (FTIR) and Raman spectroscopy of snap-frozen tissue were used for accurate assessment of the biochemical fingerprints of all cardiac chambers. FTIR and Raman spectroscopic techniques are versatile tools that allow for analysis of a multitude of samples including biologic material. Label-free samples can be analysed without any perturbation, permitting the extraction of biochemical information and images that are instrumental for diagnosis and assessment of tissue and cell architecture and functionality [2,3]. The diagnostic utility of FTIR and Raman in the HFpEF setting have not been investigated before; hence, we are pioneering the use of these technologies in the cardiovascular arena. For these reasons, we first hypothesized that the combined use of micro-FTIR and Raman spectroscopy would allow detection of novel chemical fingerprints and structural modifications that correlate with the cardiac alterations known to lead to HFpEF. We further hypothesized that during the evolution toward HFpEF, due to the different stress occurring in the four cardiac chambers, the biochemical modifications of the atria are different from those of the ventricles. Overall, our results indicate that both IR absorption and Raman scattering can sensitively probe biochemical changes at an early stage of adverse cardiac remodeling. This study demonstrated the presence of early chemical changes during the evolution of HFpEF that precede the onset of canonical and often belated signs of cardiac remodeling, such as diastolic dysfunction and cardiac hypertrophy, detectable with conventional diagnostic tools. Importantly, FTIR and Raman spectroscopy are able to detect differently regulated chemical and structural changes among the four chambers of the heart, demonstrating an unprecedented sensitivity and specificity.

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Photocurrent Generation in Supramolecular Bio-Inspired Nanoarchitectures on Gold Surface

Sascha Kubitzky,[a] Mariano Venanzi,[b] Barbara Biondi,[c] Raffaella Lettieri,[b] Marta De Zotti[c] and Emanuela Gatto[b]

[a] *Faculty of Engineering and Natural Sciences, Technische Hochschule Wildau, Wildau, 15745 (Germany)*
[b] *Department of Chemical Science and Technologies, University of Rome Tor Vergata, 00133 Rome (Italy)*
e-mail: emanuela.gatto@uniroma2.it
[c] *Institute of Biomolecular Chemistry, Padova Unit, CNR, Department of Chemistry, University of Padova, 35131 Padova (Italy)*

External stimuli are potent tools that Nature uses to control protein function and activity. In Nature, also the electron transfer (ET) properties of ET proteins are influenced by pH-induced conformational changes. In this work, a pH-controlled, reversible 3_{10}- helix to α-helix conversion (from acidic to highly basic pH values and *vice versa*) of a peptide supramolecular system built on a gold surface is described [1]. In a previous study, we succeeded in generating 3D supramolecular films on a gold surface able to generate photocurrent with high efficiency, comparable to the one obtained with non-biological systems [2]. The films have been engineered using different 2D layers, linked together by thymine–adenine DNA base pair interaction. We obtained two types of photocurrent generating films, as shown in Figure 1. Film 1 consisted of adenine linked to lipoic acid (Lipo-A) covalently bound to the gold surface, and a zinc-tetraphenylporphyrin chromophore linked to a thymine (T-ZnTPP). Film 2 had an additional noncovalently linked layer: a helical undecapeptide analogue of the natural peptide trichogin GA IV in which four glycines were replaced by as many lysines to impart water solubility and reduce flexibility. The presence of Lys residues also confers pH sensitivity to the peptide secondary structure. The peptide termini were functionalized with thymine and adenine, respectively, to enable Lipo-A and T-ZnTPP conjugation. In this contribution, we describe the effect of the pH-induced, fully reversible, conformational change on the photocurrent generation efficiency of this system. The conformational change of this modular system triggers a different self-assembly on the surface and different electronic conduction properties, leading to its possible exploitation as a pH-responsive biomolecular device. The effect of pH on the ability of the peptide SAM to generate a photocurrent was investigated, with particular focus on the effect of the pH-induced conformational change on photocurrent efficiency. The films were characterized by electrochemical and spectroscopic techniques, and were found to be very stable over time, also in contact with a solution. They were also able to generate current under illumination, with an efficiency that is the highest recorded so far with biomolecular systems.

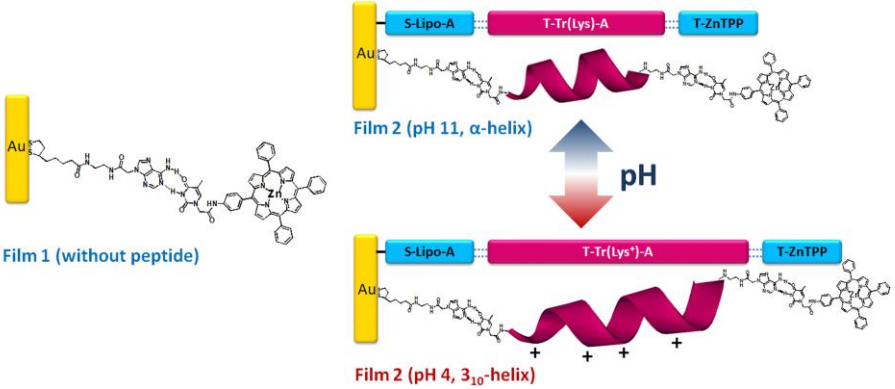

Figure 1. Chemical structures of the building blocks used for the construction of films **1** and **2** and effect of the pH on the film properties.

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Ecofriendly Isolation of Cellulose from buckwheat chaff

Daniela Caputo,[a] Caterina Fusco,[b] Angelo Nacci,[a,b] Gerardo Palazzo,[a,c] Sergio Murgia,[c,d,e] Lucia D'Accolti,[a] and Luigi Gentile [a,c]*

[a]. Department of Chemistry, University of Bari "Aldo Moro", Via Orabona 4, 70126 Bari, Italy; [b]. ICCOM-CNR, Istituto di Chimica dei Composti Organometallici, Bari Section, Via Orabona 4, 70125 Bari, Italy; [c]. Center for Colloid and Surface Science (CSGI), Sesto Fiorentino, Italy; [d]. Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy; [e]. Department of Life and Environmental Sciences, University of Cagliari, Cagliari, Italy

The separation of cellulose from vegetable sources is traditionally employing toxic chemicals, such as the Kraft pulping process. We developed a two-phase extraction process to obtain cellulose and hemicellulose from buckwheat chaff by using green solvents. In particular, three combinations of propylene carbonate (PC) and ionic liquids (ILs) in a 1: 5 ratio were adopted. The cellulose and hemicellulose were extracted into the PC / IL mixture and subsequently precipitated by water addition. The highest amount 28% of extracted material was obtained with PC-1-butyl-3-methyl imidazolium acetate (BmimAc). However, the more efficient extraction in terms of selectivity was obtained with the mixture PC- tetrabutylammonium acetate (TBAAc), where the amount of extracted material was only 10 wt%, but entirely composed of cellulose/hemicellulose with a high degree of purity, as demonstrated by the thermogravimetric analysis (TGA). The chemical composition was analyzed by FT-IR comparing the extracted material with the raw ones. Finally, self-diffusion NMR revealed the supernatants' nature obtained after the extraction process. We noticed that cellulose/hemicellulose interacts preferentially with PC in the case of PC-BdmimCl and PC-BmimAc, while interacting preferentially with the acetate group in the case of PC-TBAAc.

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Revisiting the use of probe molecules in the characterization of heterogeneous olefin polymerization catalysts by IR spectroscopy

Elena Groppo,[a] Alessandro Piovano,[a] Jelena Zarupski[a]

[a] *Department of Chemistry, INSTM and NIS Centre, University of Torino, Via Giuria 7, 10125 Torino, Italy*

Developed in the 1960s with the contribution, among others, of the Physical Chemistry school at the University of Torino, IR spectroscopy of probe molecules has become a workhorse in the surface characterization of many materials, thanks to its high sensitivity and ability to discriminate the surface sites in terms of acidity/basicity, coordination environment and accessibility. Particularly in the field of heterogeneous catalysis, the technique has become quite routine [1]. There is, however, a sector of heterogeneous catalysis where IR spectroscopy of probe molecules has been slow to make its way and where there is still a lot to do, that of olefin polymerization.

In olefin polymerization catalysts, the active sites are particularly elusive because: 1) they are generated in situ, by some activators (aluminum alkyls or their derivatives) which are added with the monomer or just before it, and are harshly reactive towards moisture; 2) they are themselves extremely instable, especially in the absence of monomer; 3) they are scarce in concentration and difficult to differentiate from the major fraction of un-activated, spectators or deactivated species; 4) often they are not fully accessible, because in strong interaction with the activator and/or its by-products, which act as hemilabile ligands displaceable by the monomer only. Finally, the research groups with expertise in spectroscopic techniques have usually a scarce knowledge of polymerization catalysis, undermining all the efforts for the characterization of the active sites. Our experience is that IR spectroscopy of probe molecules has great potential also in this field, but a real change in the paradigm of spectroscopic detection is necessary, which requires a fine control of the experimental conditions in terms of temperature at which measurements are performed, pressure, and contact time.

In this contribution, we will report a few successful examples of the use of IR spectroscopy of probe molecules in the investigation of the three main classes of heterogeneous olefin polymerization catalysts, i.e. Phillips, Ziegler-Natta and SiO_2-supported metallocene catalysts. We will show that some molecular probes (e.g. CO and acetonitrile) not only coordinate to the metal sites, but are also able to insert into the metal-alkyl bond, both in the absence and in the presence of the olefin monomer (Figure 1) [2, 3]. Hence, a careful design of the experimental protocol might allow to discriminate between active and spectator sites, and to obtain information on the kinetic of the insertion reaction, which ultimately correlates with the catalyst activity.

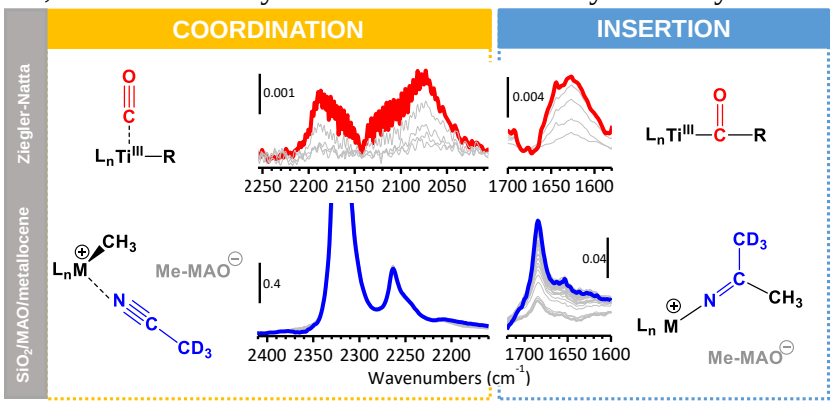

Figure 1. FT-IR spectra of CO and d-acetonitrile coordinated and inserted into the active sites of Ziegler-Natta and SiO_2/MAO/metallocene catalysts.

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Tunable Free Electron Laser and IRMPD Spectroscopy: a perfect synergy to unravel the structure and reactivity of biomolecules in the gas phase

Debora Scuderi

Institut de Chimie Physique, UMR8000, CNRS-Université Paris Saclay, 91405, Orsay, France

Tandem mass spectrometry (MS/MS) is a key methodology to study biomolecules, with the electrospray ionisation (ESI) being one of the preferred ionization techniques [1]. It is well recognized as an efficient and highly versatile analytical tool [2], however its potential has long been limited by the structural information it can provide.

For this reason, the combination of tandem mass spectrometry with IR Multiple Photon Dissociation (IRMPD) spectroscopy has become a powerful tool for 3D structural characterisation of molecular ions in the gas phase [3].

Exploiting highly intense and widely tunable Free Electron Laser (FEL), IRMPD spectroscopy allows for the derivation of the vibrational fingerprint of molecular ions under tandem mass spectrometry (MS/MS) conditions [4]. Because resonant absorption of IR photons depends on molecular vibrations, the subsequent fragmentation event is highly structure specific, revealing characteristic functional groups of the molecule.

These kinds of experiments need to be performed with high power and widely tunable IR sources, i.e. free electrons lasers (FEL) at the FELIX (Free Electron Laser for Infrared eXperiment) facility in the Netherlands [5], and at the CLIO (Centre Laser Infrarouge d'Orsay) facility in France [6]. Their temporal structure and high brightness have been shown to be particularly suitable for inducing a rapid increase of the internal energy through an efficient resonant multiple photon absorption process [7]. Furthermore, they are easily tuneable in the mid-infrared region allowing for recording the IR spectra in the so-called IR fingerprint region.

Some examples of IRMPD spectroscopy performed at the CLIO Facility in Orsay are presented here to illustrate how IRMPD spectroscopy can be exploited to learn more about the molecules in space [8], to detect posttranslation modifications [9 and refs within] or to probe the structure of UV-Induced fragmentation products [10].

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Designing Novel Nanoporous Materials for Applications in Energy and Environment. From Multi-Scale Modeling to Materials Informatics.

George E. Froudakis

Department of Chemistry, University of Crete, Greece.

http://www.chemistry.uoc.gr/frudakis

e-mail: frudakis@uoc.gr

Machine learning techniques (ML) are powerful tools already used in science and industry since their computational cost is by several orders of magnitude lower than that of the "conventional" approaches. However, their ability to provide accurate predictions strongly depends on the correct identification of those parameters (descriptors) that will allow the algorithm to effectively learn from past data. Other critical factors that affect the quality of the predictions are the size and the quality of the dataset used for the training of the algorithm as well as the correct estimation of the training size.

Aiming at both, the transferability of our model and the reduction of the training data set, we introduce 2 different classes of descriptors, based on fundamental chemical and physical properties: Atom Types and Atom Probes. The main difference from previous models is that our descriptors are based on the chemical character of the atoms which consist the skeleton of the materials and not their general structural characteristics. With this bottom up approach we go one step down in the size of the descriptors employing chemical intuition.

On parallel, an automatic procedure of identifying the appropriate size of the training set for a given accuracy was developed. A novel training algorithm based on "Self-Consistency" (SC) replaced the standard procedure of linearly increasing of the training set. Our SC-ML methodology was tested in 5.000 experimentally made MOFs for investigating the storage of various gases (H2, CH4, CO2, H2S, H2O). For all gases examined, the SC-ML methodology leads to significantly more accurate predictions, while the number of MOFs needed for the training of the ML algorithm in order to achieve a specified accuracy can be reduced by an order of magnitude. In addition, the universality and transferability of our ML model was proved by predicting the gas adsorption properties of a different family of materials (COFs) after training of the ML algorithm in MOFs.

Despite the progress in the field and the improved models that have been recently developed, ML algorithms fail to classify new materials with improved properties compared to the known ones. To the best of our knowledge the previous point has never been addressed since extrapolation is an inherent drawback of ML. The reason behind this drawback is mainly attributed to the fact that for reliable predictions of top-performing materials (materials with very high gas-adsorption capacities), ML algorithms need to be trained using materials of the same or higher performance.

In lack of such information, we propose a new methodology for the construction of artificial data (artificial MOFs) with the desired properties that will be used for ML training. This will enable ML algorithms for achieving improved predictions, in particular for high-performing materials. We demonstrate that, after using the artificial data, the capability of the ML algorithms to classify new top-performing MOFs as such, improves remarkably. We are also confident that the present methodology represents an important contribution toward the development of predictive models aiming to the discovery of new materials with outstanding properties. In addition, the main idea of this approach, can be used in many other applications of ML methodologies for overcoming the inherent problem of extrapolation.

Temperature, Pressure, and Cosolute Effects on Liquid–Liquid Phase Separation and Condensates of Proteins: Physical Chemistry and Biological Implications

H. Cinar, R. Oliva, L. Ostermeier, Z. Fetahaj, S. Mukherjee, and R. Winter

Physical Chemistry I - Biophysical Chemistry, Department of Chemistry and Chemical Biology, TU Dortmund University, Otto-Hahn Strasse 4a, D-44227 Dortmund, Germany

In recent years, it has become clear that assembly processes based on liquid-liquid phase separation (LLPS) of protein and protein-nucleic acid mixtures, acting as membrane-less organelles, play an important role in cellular self-assembly processes. We discuss the combined effects of temperature, pressure, crowding and natural osmolytes on LLPS phenomena of proteins, with a particular focus on the effect of pressure. We studied various systems undergoing LLPS, including lysozyme, crystallin, elastin, LAF1, FUS, and proteins mimicking postsynaptic densities [1-9]. X-ray and light scattering, microscopy and various spectroscopies were employed to reveal structural changes and mesoscopic phase states of the systems. Corresponding pressure-jump relaxation studies informed about the kinetics of protein droplet formation and their mechanism [8]. Strikingly, for many cases LLPSs are more sensitive to pressure than the folding of proteins, suggesting that organisms inhabiting the deep sea and sub-seafloor sediments, under pressures up to 1 kbar and beyond, have to mitigate this pressure-sensitivity to avoid unwanted destabilization of their functional biomolecular condensates. We found that crowding and particular osmolytes, such as trimethyl-amine-*N*-oxide, an osmolyte upregulated in deep-sea fish, can significantly stabilize protein droplets under pressure. We then briefly discuss the effects of aqueous two-phase systems on the pressure dependence of ligand binding and enzymatic reactions as well as the conformational dynamics of nucleic acid structures [4,6,7]. These findings are relevant for understanding cellular processes of piezophiles and might have significant bearings on biotechnological applications.

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$CuWO_4$-based photoanodes for solar energy conversion: effects of Mo^{6+} doping and coupling with $BiVO_4$

Maria Vittoria Dozzi[1], Annalisa Polo[1], Gianluigi Marra[2], Elena Selli[1]

[1] Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy.[2] Istituto ENI Donegani, Via Fauser 4, 28100 Novara, Italy.

The need for efficient visible light active oxide-based semiconductors, able to maximize solar photons absorption, is a crucial issue in solar energy conversion and storage in photoelectrochemical (PEC) applications. In this regard, $CuWO_4$ (band gap = 2.3 eV) has recently gained increasing interest in water oxidation, as a much better visible light absorber and more stable oxide alternative to wide band gap WO_3 [1]. However, an efficient use of $CuWO_4$ as photoanode material requires to overcome its severe internal charge recombination. In fact, the presence of intragap states, acting as electron traps, strongly limit the PEC performance of $CuWO_4$, as ascertained in our recent PEC investigation on this material coupled with ultrafast transient absorption analysis [2].

In this work, this fundamental issue of $CuWO_4$ photoanodes is addressed by adopting a partial Mo^{6+} for W^{6+} substitution strategy resulting in $CuW_{1-x}Mo_xO_4$ electrodes with a greatly enhanced visible light-induced photoactivity compared to pure $CuWO_4$. We optimized both the film thickness in the wide 250-700 nm range and the Mo^{6+} for W^{6+} substitution degree, by adopting a time saving preparation procedure based on the deposition of aqueous solutions of the precursors and leading to highly transparent $CuW_{1-x}Mo_xO_4$ electrodes. A thorough PEC investigation under simulated solar light irradiation, either in pure water oxidation or in the presence of $NaNO_2$ as suitable electron donor species [3], led to the identification of the *ca.* 250 nm thick $CuW_{0.5}Mo_{0.5}O_4$ film with a 1:1 W:Mo molar ratio as the best performing electrode, with a much higher photoactivity compared to pristine $CuWO_4$, thanks to the optimal compromise between light absorption and photogenerated charge carriers separation.

Furthermore, aiming at enhancing the charge carrier separation within the photoanodes, the best performing $CuW_{0.5}Mo_{0.5}O_4$ films were combined either in a heterojunction with $BiVO_4$ or in a double heterojunction with both WO_3 and $BiVO_4$. Incident photon to current efficiency (IPCE) analyses at 1.23 V vs. RHE demonstrated the definitely superior performance of both $CuW_{0.5}Mo_{0.5}O_4/BiVO_4$ and $WO_3/CuW_{0.5}Mo_{0.5}O_4/BiVO_4$ coupled systems compared to the individual components, over the entire investigated spectral range (Fig. 1). Interestingly, both heterojunction materials exhibit a better performance under irradiation from the front-side of a $BiVO_4$ layer thick enough to absorb most of the incident radiation, i.e. under conditions in which the detrimental and competitive cross-back electron-hole recombination occurring at the semiconductor/semiconductor heterojunctions is minimized.

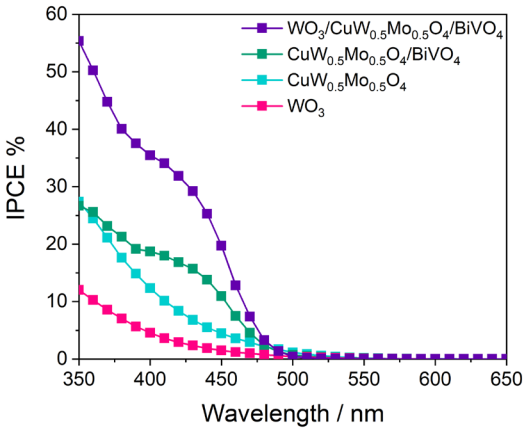

Fig. 1 *Incident photon to current efficiency (IPCE) of different photoanodes at 1.23 V vs. RHE, in 0.1 M K_3BO_3 electrolyte solution under front-side irradiation.*

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Corrosion protection in Concrete Heritage: from material design to in situ validation

Elena Messina, Maria Paola Staccioli, Simone Pagnani, Francesca Boccaccini,Cristina Riccucci, Gabriel M. Ingo, Gabriella Di Carlo

Istituto per lo Studio dei Materiali Nanostrutturati, Consiglio Nazionale delle Ricerche, Area della Ricerca Roma1, Via Salaria km 29.3, 00015 Monterotondo (RM), Italy

During the last years, an increasing attention has been addressed to the conservation of concrete monuments since they represent an important part of our heritage for their artistic, cultural or social value. To preserve them, it is necessary to develop novel solutions that are more effective than state-of-art materials and that are purposely designed for cultural heritage applications. It means that the restoration interventions should be not invasive and that the original aesthetical properties should be maintained.

At the present, one of the main degradation causes in concrete heritage is the corrosion of rebars. It is well known that the formation of corrosion products can induce mechanical stress into the concrete structure and those are typically responsible for cracks formation, spalling and detachment of the surface cover. To hinder or at least show down these deterioration processes, protective materials able to provide a reliable and long-term protection are necessary.

In order to face these issues, our research efforts have been addressed to the development of active protective materials based on stimuli responsive nanocarriers that can release a corrosion inhibitor only in a degrading environment. This approach, previously used for the protection of copper alloys [1-2], was proposed and optimized for the conservation of concrete monuments within the H2020 InnovaConcrete project.

A proper selection of corrosion inhibitors for steel rebars was carried out by assessing their efficacy in simulated concrete pore solutions. Silica and layered double hydroxide (LDH) nanocarriers were functionalized with the selected inhibitors to achieve a tailored release of protective molecules under pH variations or in the presence of chloride ions. The inhibitor loading and the release conditions were evaluated. The results showed that, by selecting an appropriate nanocarrier, it is possible to tune the inhibitor release, which is triggered by alkaline environments for silica-based materials and by chloride ions for LDH-based materials. Our findings confirm that using silica or LDHs, it is possible to obtain a complementary protective action [3].

Moreover, the nanocarriers loaded with corrosion inhibitors were incorporated into new consolidants thus producing innovative multifunctional systems. After laboratory validation, the optimized products were applied on XX century concrete monuments identified as representative case studies and situated in Italy, Spain and Poland. The in situ validation is still ongoing and the results achieved so far are promising.

This work has been carried out within the InnovaConcrete project funded by the European Union's Horizon 2020 Research and innovation programme under the grant agreement No 760858.

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From Molecules to Supracolloidal Atomium like Superstructures: Building from the Bottom-Up with Steroidal Amphiphiles

Jacopo Cautela [a], Björn Stenqvist [b], Karin Schillén [b], Domagoj Belić [b], Linda K. Månsson [b], Fabian Hageman [c], Maximilian Seuss [d], Andreas Fery [d], Jérôme J. Crassous, [b,c] and Luciano Galantini[a]

[a]Department of Chemistry, Sapienza University of Rome, Italy; [b]Division of Physical Chemistry, Department of Chemistry, Lund University, Sweden; [c]Institute of Physical Chemistry, RWTH Aachen University, DE-52056 Aachen, Germany; [d]Leibniz-Institut für Polymerforschung e.V. Institut für Physikalische Chemie und Physik der Polymere, DE-01069 Dresden, Germany

At the nano- and micro-scales, molecules and colloidal particles can arrange in diverse frameworks to form basic biological units, like cells, and extended superstructures, according to fundamental principles of hierarchical assembly.[1,2] Within this scenario, rationally designed molecules obtained by chemical modification of natural steroidal surfactants allow a controlled self-assembly into supramolecular aggregates at the nanoscale (Fig. 1a,b), and to rationally direct the association of these and other building blocks to specific functional superstructures at supracolloidal level.[3,4] The effort to direct the supramolecular and supracolloidal association into Atomium like superstructure is described (Fig. 1c,d). We demonstrate that this superstructure can be implemented by engineering specially customized bile salt derivative-based supramolecular tubules that exhibit a highly specific interaction with polymeric microgel spheres at their extremities thanks to their scroll-like structure. This design allows for hierarchical supracolloidal self-assembly of microgels and supramolecular scrolls into a regular framework of "nodes" and "linkers". The supramolecular assembly into scrolls can be triggered by pH and temperature, thereby providing a colloidal smart assembly with features of center-linker frameworks as those found in molecular metal–organic frameworks.

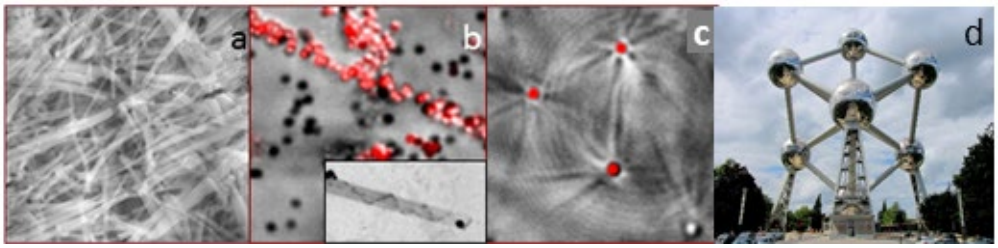

Figure 1. Supramolecular (a) and supracolloidal structures (b,c) and Atomium (d).

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Design for biointerface engineering

Roberto De Santis

Institute of Polymers, Composites and Biomaterials, Italian National Research Council, IPCB-CNR, Naples, Italy

The need for functional scaffolds or prostheses which are able to replace or repair tissues or organs is overwhelming. Over the past few years, synthetic polymers have become popular in many applications and several advances are being made for the development of novel devices for biomedical applications. Additive manufacturing allows for the design of advanced prostheses and scaffolds with tailored architectures, mechanical and functional properties. Conventional fabrication methods do not allow to strictly control the pore size and geometry, as well as the spatial distribution of pores. Many works have also evidenced contemporary tendencies in the use of non-degradable scaffolds and mesenchymal stem cells in regenerative medicine.

Design is the main creative activity of engineering. In general, the engineers may benefit from a series of steps to develop functional products and processes. Although several generalized and simplified models have been reported in the literature, the common steps of the engineering design process involve research, design requirements, feasibility, concept generation, preliminary design, detailed design, design for manufacturability, and production planning. Conceptual design is considered the first phase of design, providing a description of the proposed device in terms of a set of integrated ideas and concepts with a special focus on its function, structure and behaviour.

A surface chemical way of thinking is often integrated with appropriate design strategies and advanced technologies when taking into account approaches, products and applications in the biomedical field.

With regard to tissue engineering, additively manufactured scaffolds with controlled structural and surface properties may be also developed. The efficacy of a two-step procedure for peptide grafting has been frequently reported. The analytical quantification of functional groups and/or peptides at the interface and the assessment of the mechanical properties at different level clearly play a crucial role in the optimization of the 3D structures.

A combination design of time-dependent magnetic field and magnetic nanocomposites has also been carried out, with a special focus on the potential to guide cell behaviour.

Accordingly, the combination of design methods with additive manufacturing and functionalization/bioactivation strategies can lead to the development of engineered biointerfaces and 3D biomimetic devices. Thus, current researches aim at providing a further insight into the design for biointerface engineering.

New trends in the development of biomedical implants with multifunctional surfaces

Julietta V. Rau

Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche (ISM-CNR), Via del Fosso del Cavaliere, 100 - 00133 Rome, Italy

In a near future, a substantial increase of implant demand is expected due to a dominant demographic phenomenon - population ageing and rising of life expectancy. The main requests for implants are their good osteointegration and long-term stability. For this purpose, metallic implants should be coated with biomimetic functional biomaterials improving their properties, and consequently, their integration with the surrounding bone tissue. In this work, the results obtained for novel biomaterials possessing various functional characteristics designed for coatings on titanium and on biodegradable metal alloys are reported. In the case of biodegradable implants, the focus points are controlling their degradation rate and imparting them with bioactivity properties [1]. The developed coating materials are based on substituted calcium phosphates [2,3] and bioactive glasses of innovative composition [4,5], containing trace elements with therapeutic functions, which are involved in natural bone and connective tissue formation. The effect of trace elements on cell functions is dose-dependent and its release is carefully tuned. Various aspects of coatings' development, among them antibacterial properties, are focused. The coatings' deposition procedure and corresponding conditions are selected. Throughout characterization of the coatings is performed; structural, morphological, mechanical, wetting contact angle, magnetic properties, electrochemical tests in simulated body fluid, etc. are reported. *In vitro* bioactivity, microbiology and cell tests results are presented, focused on material-cell interactions, and, in particular, on trace ion influence. The obtained results suggest that novel biomimetic nanostructured materials can be particularly relevant for new strategies for tissue replacement and regeneration.

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Reversible and low-cost CO_2 capture by quaternary-ammonium-functionalized aromatic polymers

Cataldo Simari [a,b]; Alfonso Policicchio [c,d,e]; Ernestino Lufrano [a]; Giuseppe Conte [c,d,e]; Raffaele Giuseppe Agostino [c,d,e]; Isabella Nicotera [a,b].

[a] Dept. of Chemistry and Chemical Technology, University of Calabria, 87036 Rende (CS), Italy;[b] National Reference Centre for Electrochemical Energy Storage (GISEL)—INSTM, Via G. Giusti 9, 50121 Firenze Italy [c]Dept. of Physics, University of Calabria, 87036 Rende (CS), Italy.[d] CNISM – Consiglio Nazionale Interuniversitario di Scienze Fisiche della Materia, Via della Vasca Navale, 84, 00146, Roma, Italy[e] CNR-Nanotec, c/o Università della Calabria, Via Ponte P. Bucci, Cubo 31C, 87036, Arcavacata di Rende, CS, Italy

Meeting the increasing global demand for energy while simultaneously facing the climate change due to anthropogenic carbon dioxide (CO_2) has become the great paradox of the 21st century [1]. If we really want to meet both these criteria, the development of CO_2 capture, use, and storage technology has become imperative for sustainable energy infrastructure development.
Regardless of the maturity if the various type of carbon dioxide capture technologies, the amine-based ones seem, so far, the most promising strategy to develop efficient decarbonation's processes. Indeed, primary, secondary and tertiary amines as well as quaternary ammonium groups can rapidly and reversibly react with CO_2, making them ideal for the separation of CO_2 from a mixture of gasses [2].
Unfortunately, the current technology is still based on the use of amine solutions which typically implies several issues during operation, including high energy consumption during the desorption stage, low absorption capacity, oxidative and thermal degradation, loss of the amine due to poisoning, and piping corrosion [3]. This makes the overall process quite expensive.
Against this background, the development of membrane technology can effectively represent a competitive way of the decarbonation, since can potentially conjugate remarkable thermal, chemical and mechanical resistance with high CO_2 affinity [4].
In the presentation, some preliminary data will be discussed concerning the design, synthesis and characterization of quaternary-ammonium-functionalized Polysulfone to be employed in the CO_2 capture processes. The physico-chemical and gas transport properties were deeply characterized by two different and complementary techniques: an isothermal gas adsorption study using a Sievert type (volumetric) apparatus at RT and in the range of 0 - 15 bar (solid polymer conditions) and the pulse field gradient (PFG) Nuclear Magnetic Resonance (NMR) spectroscopy. This latter method is able to effectively clarify the confinement effects and molecular interactions with the polymer that greatly influence the mobility of the CO_2, thus enabling a profound comprehension of the structure-performance relationship in such a complex system.

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Development of a thermodynamic and kinetic model for passivemigration of ion carriers across lipid bilayers

Mariano Andrea Scorciapino,[a] Giacomo Picci,[a] Claudia Caltagirone[a]

[a]*Chemical and Geological Sciences, Università degli Studi di Cagliari, Monserrato, Cagliari, Italy.*

Homeostasis is crucial for cell functioning and relies on both passive and active transport processes. In recent years, a large number of ion carriers (in particular for the transport of chloride and bicarbonate) have been reported in the literature [1]. They have been shown to facilitate ions exchange across lipid bilayers and some of the most interesting compounds also advanced to successful biological tests in-vitro. Selective toxicity against cancer cell-lines, antimicrobial activity and treatment of channelopathies are important possible applications. Quantitative understanding of the interplay between the numerous underlying equilibria would open the route to supramolecular medicinal chemistry, which appears promising but still at early stage. Despite several mechanisms have been put forward and corroborated by experiments and atomistic simulations, and despite correlation with parameters such as logP and adduct formation constant in solution have been shown, many aspects of the overall transport process are still unclear. We are developing an integrative thermodynamic and kinetic model to take into account the chemical equilibria on both sides of the lipid membrane and the diffusion of the different species across it [2]. We wrote the corresponding algorithm to simulate the experimental curves of ion release from lipid vesicles as a function of time. By working on selected benchmark cases, we include as many experimentally derived constants as possible, in order to use only a few fitting parameters. The goal is a computational tool to allow rapid investigation of the relative weight of many different parameters on transport efficiency, so to virtually compare a variety of candidates before moving to more time- and resources-consuming lab campaigns.

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Fabrication and spectroscopic investigation of Quantum Dots dimers

Carlo Nazareno Dibenedetto[a,b,*], Elisabetta Fanizza[a,b], Liberato De Caro[c], Rosaria Brescia[d], Annamaria Panniello[b], Raffaele Tommasi[e,b], Chiara Ingrosso[b], Cinzia Giannini[c], Angela Agostiano[a,b], Maria Lucia Curri[a,b], Marinella Striccoli[b]

[a] Dipartimento di Chimica, Università degli studi di Bari ''Aldo Moro'', Via Orabona, 4 - 70125 Bari (Italy);
[b] Istituto per i Processi Chimico Fisici del CNR (IPCF-CNR), Via Orabona, 4 - 70126 Bari (Italy);
[c] Istituto di Cristallografia del CNR (CNR-IC), Via Amendola, 122/O - 70126 Bari (Italy);
[d] Istituto Italiano di Tecnologia (IIT), Via Morego 30 - 16163 Genova (Italy);
[e] Dipartimento di Scienze Mediche di Base, Neuroscienze e Organi di Senso, Università degli Studi di Bari "Aldo Moro", Piazza G. Cesare 11 - 70124 Bari (Italy)

The investigation of the mutual interaction among colloidal quantum dots (QDs), when organized in molecular assemblies is of great interest for designing QD based optoelectronic devices with high performances. In particular, the coupling taking place when only few QDs interact at short interparticle distance is relevant to better promote the electron/energy transfer processes arising in such molecular assemblies, for new technological applications.
Heterodimers composed by CdSe QDs of two different sizes,[1] and analogous homodimers formed by QDs of the same size,[2] connected by short alkyl chain dithiols, are fabricated in solution. Varying the chain length of the bifunctional linker from nanometer to sub-nanometer range, it is possible to fine tuning the interparticle distance. An exhaustive spectroscopic investigation allows to rationalize the interaction mechanisms between the QDs, ranging from charge transfer/wavefunction delocalization to energy transfer, depending on their separation distance, size and energetic levels position. The findings evidence the potential of the heterodimers in terms of transfer rate in application where a high charge transfer/wavefunction delocalization is required, taking advantage from the cascade-like energetic levels in the contact zone. On the other hand, FRET architectures would strongly benefit from the use of homodimers that are able to couple more efficiently by means of energy transfer mechanism, thanks to quasi iso-energetic electronic levels.

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Forces between nanoparticles at the air/water interface: the role of the ligand chain length

Giovanni Li Destri, Roberta Ruffino, Nunzio Tuccitto and Giovanni Marletta

a) Department of Chemical Sciences, Università degli Studi di Catania, Viale A. Doria 6, 95125 Catania, Italy.
b) Laboratory for Molecular Surfaces and Nanotechnology-CSGI, Viale A. Doria 6, 95125 Catania, Italy

In the last years, the assembly of nanoparticles (NPs) into monolayers at liquid interfaces has been at the focus of intense experimental and theoretical research given the possibility to finely tailor the monolayer structure and properties via control of the environmental conditions.[1] However, deeper understanding of the interfacial inter-particle interactions driving the assembly after NP adsorption or spreading is needed, given their critical role for the fine tuning of the monolayer structure and properties.[2]
We have recently shown that, by simultaneously measuring the work exerted to compress a NP monolayer in a Langmuir trough and the compression-induced inter-particle distance reduction via synchrotron radiation grazing incidence small angle X-ray scattering (GISAXS), it is possible to quantitatively measure inter-particle forces and their inter-particle distance dependence.[3]
In the present work, we further extend our investigation by measuring the inter-particle forces acting between negatively charged silica NPs decorated by cationic surfactants bearing different chain length.
The Langmuir isotherm reported in figure 1A shows that the compression work to be exerted increases with the surfactant chain length. Additionally, the inter-particle distance is, especially for the three longest surfactants, independent on the chain length at any compression degree (see Figure 1B). These findings suggest that, in the present case, the main contribution to the compression work relates to steric repulsions increasing with chain length. Therefore, our approach appears very promising to enable, for the first time, the quantitative determination of interfacial steric forces and to their dependence on the chain length.

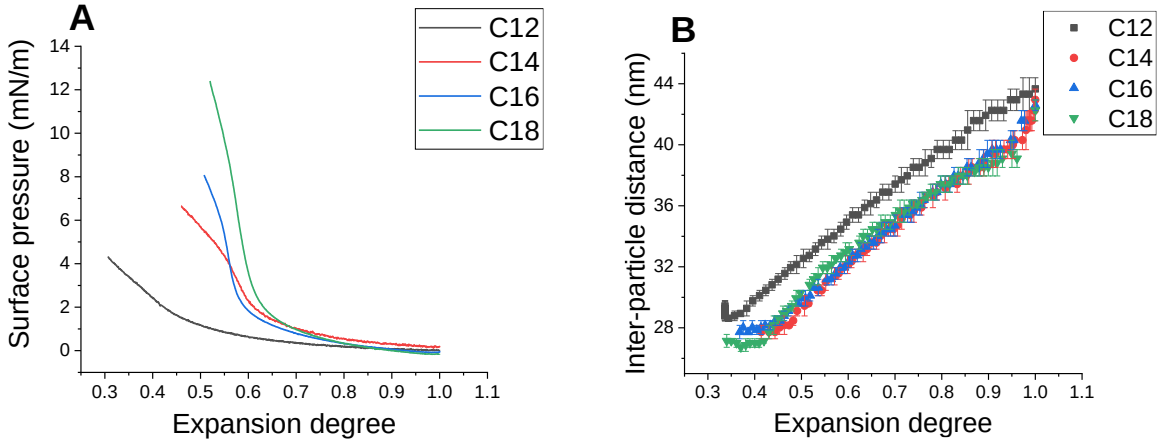

Figure 1. Surface pressure vs Area compression isotherm of 0.1% wt silica NPs decorated with various surfactants (A) During compression, the inter-particle distance determined by GISAXS progressively decreases (B).

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Interplay between inter- and intraparticle interactions in bi-magnetic core/shell nanoparticles

A. Omelyanchik[a,b], S. Villa[a], F. Canepa[a], G. Singh[c], M. Vasilakaki[d], G. Margaris[d], K. N. Trohidou[d] and D. Peddis[a,d]

[a]Department of Chemistry and Industrial Chemistry (DCIC), University of Genova, Genova, Italy; [b]Immanuel Kant Baltic Federal University, Kaliningrad, Russia; [c]Department of Materials Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway; [d] Institute of Nanoscience and Nanotechnology, National Center for Scientific Research Demokritos, Athens 15310, Greece; [d]Istituto di Struttura della Materia, CNR, 00015 Monterotondo Scalo, (RM) Italy

Bi-magnetic nanoparticles of magnetic oxides with a core/shell structure are widely investigated due to their potential use in various applications, ranging from electronics to biomedicine [1]–[3]. The surface/interface effect and interparticle interactions strongly affect their magnetic properties and thus they should be considered to design materials with desired properties. However, all those effects have complex nature, and it is not trivial to consider them at the design step of materials.

This work focuses on the study of the magnetic properties of bi-magnetic core/shell nanoparticles of cobalt ferrite (CFO) and nickel ferrite (NFO), also in the inverse configuration. The growth of a magnetically soft NFO shell affects the hard properties of the CFO seeds with a decrease of $\mu_0 H_C$ from ~1.3 to 0.8 T. On the contrary, the magnetically harder shell increases the coercivity of the NFO seeds from ~0.025 to 0.03 T. These changes cannot be explained quantitatively by a classical additive rule: a strong influence of the architecture was revealed in a clear interplay among intraparticle (i.e., proximity effects) and interparticle interactions.

This effect has been investigated by the remanent plot's technique. Then we applied the Monte Carlo simulation method to better understand the effect of different factors and for the first time in the core/shell system, the contribution of proximity effects in ΔM-plot has been highlighted. Implementation of this model allows one to design the material with desired magnetic properties.

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XAS Study of Molecular Coated Manganese Zinc Ferrite Nanoparticles

Maryam Abdolrahimi[a,b], Souad Ammar Merah[c], Carlo Meneghini[a], Davide Peddis[b,d]

[a] Università degli Studi Roma Tre, Via della Vasca Navale 84, 00146 Roma - RM, Italy; [b] Consiglio Nazionale delle Ricerche, via Salaria Km 29.300, 00015 Monterotondo Scalo (Rm), Italy; [c] Università di Genova, Via Dodecaneso 31, I-16146 Genova, Italy; [d] Universite de Paris, CNRS UMR-7086, Rue Jean-Antoine de Baïf 15, F-75205 Paris, France.

Molecular coating of magnetic iron oxide nanoparticles by organic molecules is attracting intensive research owing their possible biomedical applications such as magnetic drug targeting, cancer treatment (hyperthermia), enzyme immobilization, or magnetic resonance imaging [1]. Several authors have shown that the influence of different ligands bonded at the surface of magnetic nanoparticles (NPs) plays a significant role in the magnetic properties of the NPs. In this landscape Manganese Zinc ferrite NPs (MZFO) are chosen owing their high saturation magnetization and low resistivity. In addition, Mn-Zn ferrites are very important ferromagnetic ceramics, particularly for application at high frequencies. Encapsulating the MZFO NPs core with opportune ligand shells allows to modify the magnetic interactions between magnetic cores and the molecular shells providing new features valuable for specific applications, influencing both surface magnetic disorder and single ion magnetic anisotropy [2].

In this study, a set of core-shell magnetic NPs based on MZFO magnetic cores with averagely 7 nm diameter, is coated with three different organic molecule shells: Dopamine (dop), Oleylamine (ole) and Citrate (cit). The MZFO NPs crystallographic phase and morphological characterization has been carried out by x-ray diffraction and TEM. The chemical interactions of the core with the organic shells were accurately characterized by FTIR spectroscopy and TGA technique. The magnetic response of the MZFO NPs (bare and coated) as a function of magnetic field and temperature was characterized by DC magnetization (performed with SQUID). The results showed that the nanoparticles coated with Dopamine depict anomalous magnetic response with an unsaturated magnetization suggesting smaller magnetic cores despite the same synthesis procedure for all the samples. Further details have been obtained by XAFS, which provided details about local atomic structure around Fe, Mn and Zn atoms of all MZFO samples. The Fe, Zn and Mn K-edge XAFS data analysis revealed a strong chemical interaction between dopamine molecules and the NPs which removes the metals from the MZFO core, this effect being especially evident for Mn, also for the citrate molecules (figure 1). Such interaction between organic molecules and MZFO NPs is responsible for the magnetic behavior modifications and must be carefully considered in these core-shell systems.

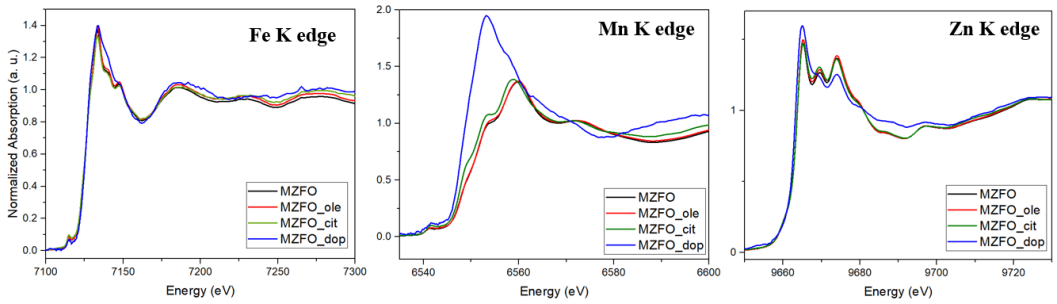

Figure 1: XAS signals measured on MZFO samples (coted and bear) at the Fe, Mn and Zn K-edges

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Hybrid Spinel Iron Oxide Nanoarchitecture Combining Crystalline and Amorphous Parent Material

Sawssen Slimani[1,3,4], Giorgio Concas[2], Francesco Congiu[2], Gianni Barucca[5], Nader Yaacoub[6], Alessandro Talone[4,7], Mourad Smari[3] , Essebti Dhahri[3] , Davide Peddis[1,4], Giuseppe Muscas[2].

[1] *Università di Genova, Dipartimento di Chimica e Chimica Industriale, nM2-Lab, Via Dodecaneso 31, I-16146, Genova, Italy*; [2]*Department of Physics, University of Cagliari, Cittadella Universitaria di Monserrato, S.P. 8 Km 0.700, I-09042 Monserrato (CA), Italy.*; [3]*Laboratoire de Physique Appliquée, Faculté des Sciences, Université de Sfax, B.P. 1171, 3000 Sfax, Tunisie.*; [4] *CNR, Istituto di Struttrua della Materia, nM2-Lab, Monterotondo Scalo (Roma), 00015, Italy;* [5]*Università Politecnica delle Marche, Dipartimento di Scienze e Ingegneria della Materia, dell'Ambiente ed Urbanistica, Via Brecce Bianche 12, 60131 Ancona, Italy.*[6]*IMMM, Université du Main, CNRS UMR-6283, Avenue Olivier Messiaen, Le Mans 72085, France.* [7]*Università degli Studi 'Roma Tre', Dipartimento di Scienze, Roma, Italy.*

Abstract

When preparing nanostructured magnetic materials, the presence of an amorphous component is often considered a weakness of the synthesis method. This stems from the fact that the amorphous fraction is often pictured as a “dead” magnetic component, showing little to no contribution to the magnetic properties. e.g., saturation magnetization. Here we propose a hybrid-structured nanoarchitecture that combines crystalline cobalt ferrite and the amorphous parent material. This nanocomposite was prepared by coprecipitation method [1] without further steps employed after the main synthesis process. Transmission electron microscopy (TEM) analysis evidenced small crystalline particles ($\langle D_{TEM} \rangle \sim 3$nm) embedded in amorphous matrix. By Applying the Debye-Scherrer formula to the most intense reflection of the XRD pattern peak confirm an average size of the crystalline structure of about 3 nm. The investigation of the magnetic properties by SQUID magnetometer and the magnetic structure by means of Mössbauer on the crystalline/amorphous sample pointed out that the amorphous phase contributes partially to the total magnetic moment accompanied by a strong variation in the anisotropy (i.e., Hc =1.3(1) T, at 5K). Cross-checking the obtained information from structural and magnetic characterization, we have proposed a micromagnetic model using the software Mumax3, which sheds light on the contribution of each component elucidating the active role of the amorphous phase as a "non-dead magnetic phase", but a magnetically canted structure, with low effective magnetization and very large magnetic anisotropy coupled with the regular core structure.[2]

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Porous materials for hybrid functional nanocomposites: metal and organic nanowires confined in zeolites and mesoporous silica

Marco Fabbiani[*a], Rossella Arletti[b], Mario Santoro[c], Francesco Di Renzo[a], Romain Viennois[a], Olivier Cambon[a], Jerome Rouquette[a], Frederico Alabarse[d], Andrea Ponzoni[e], Julien Haines[a]*

[a] ICGM, Univ Montpellier-CNRS-ENSCM, Montpellier, France.[b] Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Modena, Italy.[c] LENS, INO-CNR, Sesto Fiorentino, Italy.[d] XPRESS Beamline, Elettra Sincrotrone Trieste, Basovizza, Italy.[e] INO-CNR and Dipartimento di Ingegneria dell'Informazione, Università degli Studi di Brescia, Brescia, Italy.

The creation of novel functional materials is a technological need and a scientific challenge for the production of innovative systems able to face the requirements of many application fields. Cooling technologies are useful in many fields related to daily life (domestic refrigeration, computer cooling, air conditioning etc.) as well as high technology (cooling of optoelectronic devices, superconducting devices, thermal management of electronic devices etc.) In this, all-solid technologies based on the thermoelectric effect such as Peltier cooling devices represent a real alternative, as they have no moving parts, are compact and reliable despite their limitations, so far mainly due to their insufficient performance and their rather high cost. While typically used alloys can be toxic and expensive, Bi1-xSbx alloys have a strong potential for cooling applications. Therefore, the insertion of the metallic component inside of a porous structure, such as zeolite channels and silicas pores, could improve the thermoelectrical properties with respect to the bulk material. The specific aims are the decrease of thermal conductivity and the increase of the Seebeck coefficient by exploiting the quantum confinement of the metal phase [1].
Besides metals, also organic molecules are of interest when confined in a zeolite channel. The possibility of insertion and reaction of molecules inside an organized scaffold can lead to new properties of both the inorganic host structure and the organic guest molecule. Exploiting the wide variety of the organic functions, ranging from multiple C-C bonds to the presence of heteroatoms, a multitude of composites can serve to the different purposes of the ever-growing demand of modern efficient materials. In particular, the use of unsatured hydrocarbons monomers allows for the formation of polymers within the porous structure exploring different ranges of temperature and pressures [2]. These hybrid systems are of interest for applications such as gas sensor materials exploiting the possibility to form conducting polymers. A promising one is found in the AlPO-54/polyphenylacetylene (PPhA) system for which the polymerization of the PhA molecules was obtained [3].
The systems are studied and characterized by infrared, Raman and nuclear magnetic resonance spectroscopy, transmission electron microscopy and X-ray neutron diffraction both at ambient pressure and at high pressure to provide a rich description of the host-guest interactions.

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Surfactant vesicles and polysaccharides interactions with cellulose nanocrystals

Grazia M. L. Messina[a], Evdokia K. Oikonomou[b], Laurent Heux[c], Jean-François Berret[b], Giovanni Marletta[a]

[a]Laboratory for Molecular Surface and Nanotechnology (LAMSUN), Department of Chemical Sciences, University of Catania and CSGI, Viale A. Doria 6, 95125 Catania, Italy[b]Université de Paris, CNRS, Matiére et Systémes Complexes, 75013 Paris, France[c]Centre de Recherches sur les Macromolécules Végétales, CS 40700, BP 53, 38041 Grenoble Cedex 9, France

The primary goal of soft interfaces is to achieve controlled, switchable or stimuli-responsive interactions with respect to its (liquid or solid) environment.

One area where soft interfaces are important is that of the deposition of actives on textiles.

Concentrated fabric conditioners are water-based formulations containing 10 wt% of cationic surfactants that are deposited on textile fibers during the rinse cycle in a washing machine to make them smoother and softer to touch. The surfactants assembly into micron sized vesicles, that ensure the stability of the dispersion and act as carriers for oils and fragrances onto the cotton.

To simulate textile we used CNC as a cotton fiber model, assessing the adsorption of topical formulations of double-tailed surfactants and polysaccharides.

CNCs are the crystalline part of cellulose fibers and are available as bulk dispersions. Their shapes are mostly rod-like and their sizes around 100 nm. In recent years, CNC coated substrates have received increasing attention with regard to surface techniques, mainly for testing adsorption properties of polymers and proteins. The polysaccharides are cationic guar gum (C-Guar) and a hydroxypropyl guar (HP- Guar), both extracted from the seeds of cyamopsis tetragonalobus plant, and used as additives. Surfactant formulations modified with C-Guar and HP-Guar were shown to display remarkable softness performances as compared to the additive-free benchmark.

In this work, we use Scanning Probe Microscopy, both in AFM and Force Spectroscopy modes, QCM-D and ellipsometry to monitor the adsorption of surfactant vesicles and polysaccharides onto model cellulose substrates and the correlation between the structure of the deposited layer and the "softness" properties. In particular, QCM-D allowed to determine the adsorption kinetics of the surfactants and guar, as well as the energy dissipation properties of the adlayer, i.e., the viscoelasticity of the adsorbed layer as a whole, while Force Spectroscopy allowed to determine Young modulus, i.e. stiffness, at the nanoscale, of the global cellulose-surfactant-guar construct.

The results show that the softness performance depends on the mass adsorbed at the cellulosic interfaces. In the presence of guars, the adsorbed quantities measured by QCM-D are less (by 60%) than the sum of the respective amounts of each component, but the structure of the soft interface is more homogenous and rigid.

Overall, the results suggests synergistic effects between surfactants and these particular polysaccharides, and that the guars could also contribute to the softness mechanism. The experimental results highlight that surface techniques coupled with robust CNC coated substrates are promising for studying interactions of the many components of current conditioner formulations with cotton.

Highly efficient green inkjet printed nanostructured electrodes and SERS substrates

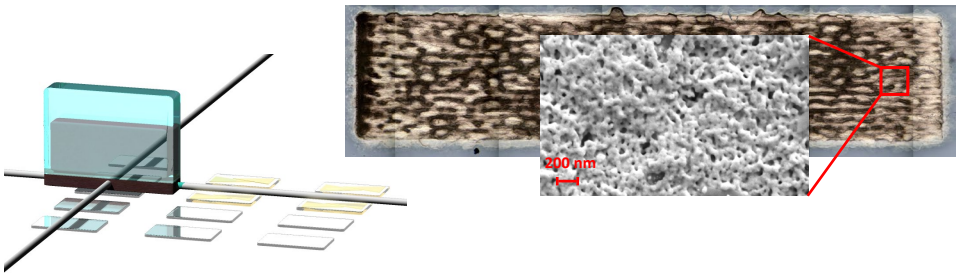
Simona Ricci,[a] Marco Buonomo,[b] Moreno Meneghetti,[a] Lucio Litti[a]

[a]*Department of Chemical Sciences, University of Padova, Via Marzolo, 1, 35131, Padova, Italy, simona.ricci@unipd.it*
[b]*Department of Informatic Engineering, University of Padova, Via Gradenigo 6/b 35131, Padova, Italy*

Nanostructured metal thin films play an active role in a broad range of applications, such as electronic, optical and magnetic devices.[1] Thus, the investigation of alternative production methods to conventional ones, which require a high specialized laboratory, such as lithography, is of paramount importance. In this regard, inkjet printing represents a cost-effective, solution-processed, and sustainable technique for thin films patterning. However, printable inks have to fulfil precise characteristics in terms of viscosity, surface tension and density, which still discourages its widespread diffusion.[2]

Gold nanoparticles (AuNPs) are widely employed in nanotechnology, due to their remarkable electronic and optical properties, biocompatibility, and ease of functionalization and preparation.[3] Laser ablation synthesis in liquid solution (LASiS) is a green and versatile technique extensively used for the preparation of a broad kind of nanomaterials.[4]

Different AuNP-based inks for inkjet printing of gold thin films are presented. A thorough study was conducted on the printed gold films aiming at characterising their optical and electrical properties along with their morphology. A surprisingly remarkable conductivity without the need for post thermal treatment as well as excellent SERS features were achieved, making a step forwards on a more green, efficient, and scalable gold thin films production.



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Ag nanoflowers as single particle SERS active platform

M. Condorelli[a], L. D'Urso[a], G. Compagnini[a]
[a] *Dipartimento di Scienze Chimiche, Università degli Studi di Catania*

For several years, Surface-enhanced Raman scattering (SERS) has received much attention from all scientific communities due to the high range of non-destructive applications it is involved in. Raman spectroscopy has been successfully employed in biosensing [1], in-situ catalysis study, archeology, and so on. Anyway, the low sensitivity of the technique has hindered its application when low concentrations are involved. For this reason, the magnification of Raman signals due to the SERS effect is the core of scientific research. As a matter of the fact, the maximum enhancement calculated theoretically is 10^{14} [2] that corresponds to a limit of detection (LOD) of attomoles. Up to now a lot of different types of metallic nanoparticles were produced trying to match the theoretical enhancement. However, the relative low stability and homogeneity of the SERS substrate hinder its practical applications. In this work, we present a novel approach to the study of the enhancement factor of SERS active substrates. We synthesize Ag Nanoflowers (AgNFs) which are spherical silver micro-particles with a diameter of 2 μm with a nano-rough surface [3] (figure 1 (a)). Such Ag NFs are spin-coated onto a silicon substrate. Due to the bigger dimension of Ag NFs by using a Micro-Raman we can study the single micro-particle Raman enhancement. The SERS properties at single-particle level were studied by using two standard molecule, Rodhamine 6G (figure 1(b)) and 4-mercaptobenzoic acid (4-MBA). Thanks to the systematic study of the enhancement for several-single Ag NFs, we find an enhancement factor in the order of 10^8- 10^9 which result to be 3 order of magnitude higher than the classical Ag sphere (AgNPs).

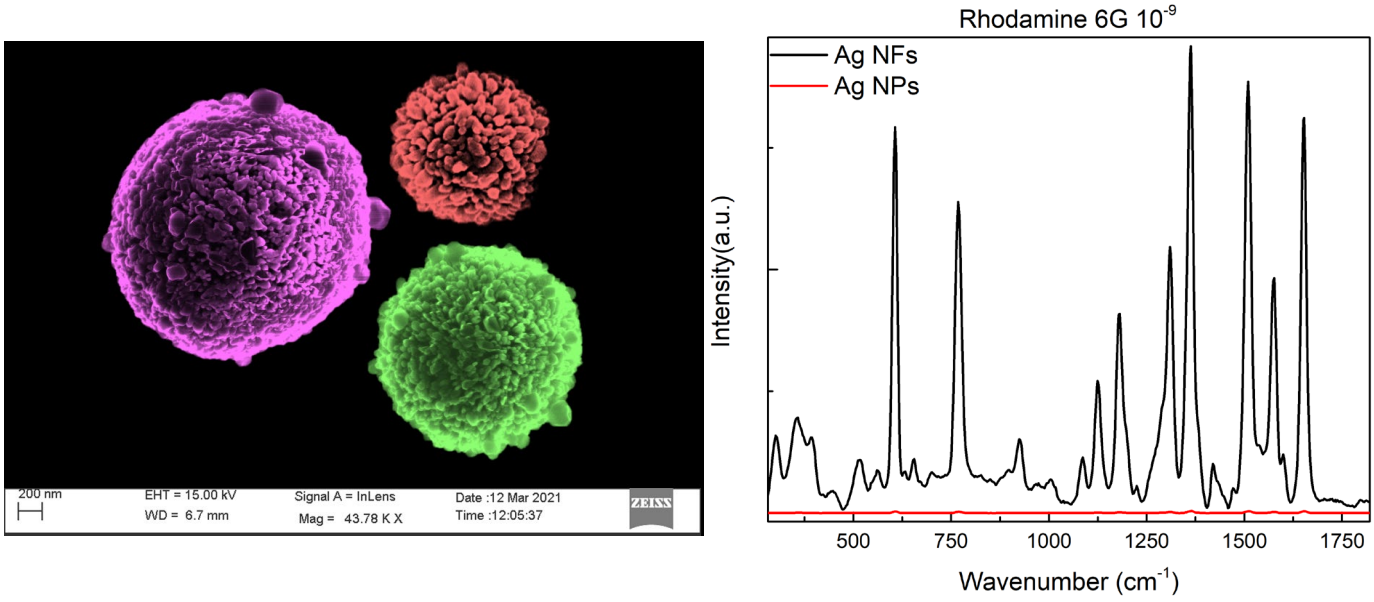

Figure 1: (a) SEM image (false color) of Ag NFs, (b) comparison between SERS spectra of Rhodamine 6 G in presence of Ag NFs(black) and Ag NPs (red).

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^{57}Fe Mössbauer Spectroscopy and DC magnetometry for the identification of Fe-bearing ultrasmall nanophases in inorganic ordered porous matrixes

Valentina Mameli[a,b], Claudio Cara[a,b], Marco Sanna Angotzi[a,b], Mirko Antonio Vacca[a,b], Anna Musinu[a,b], Daniel Nižňanský[c], Carla Cannas[a,b,d]

[a] Department of Chemical and Geological Sciences, University of Cagliari, Cittadella Universitaria S.S. 554 bivio per Sestu, 09042 Monserrato, Cagliari, Italy; [b] Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Cagliari Unit, Via Giuseppe Giusti, 9, 50121 Firenze, Italy; [c] Department of Inorganic Chemistry, Charles University, Hlavova 8, 128 00 Prague 2, Czech Republic; [d] Consorzio per la promozione di Attività Universitarie Sulcis-Iglesiente (AUSI), Centro di Ricerca per l'Energia, l'Ambiente e il TErritorio (CREATE), Palazzo Bellavista Monteponi, 09016 Iglesias, Italy

Studying ultrasmall nanophases diluted within a matrix of variable complexity might be challenging when conventional techniques such as X-ray diffraction and electron microscopy do not assure their identification, provide information on their morphology and their changes when specifically applied in a process. Nevertheless, when the characterization is focused on Fe-bearing phases, ^{57}Fe Mössbauer Spectroscopy and DC magnetometry have been proved to be powerful lab-available techniques to answer these questions, even in diluted and complex natural composites.[1] Indeed, ^{57}Fe Mössbauer Spectroscopy permits to extract mass-averaged information on both structural and magnetic properties of iron species (oxidation state, coordination chemistry and magnetic behavior), whereas DC magnetometry provides temperature and magnetic field dependences, estimation of domain sizes, evidences of magnetic transitions, interactions, and coupling phenomena.
In this contribution, ^{57}Fe Mossbauer Spectroscopy and DC magnetometry are applied for the study of synthetic nanocomposites built by growing ultrasmall (2-5 nm) iron oxides nanoparticles within the mesopores (SBA15, MCM-41, MCM-48) of amorphous silica and crystalline titania (anatase) matrixes and within macropores of a macroporous ordered siliceous foam (MOSF).[2–5] The study of the synthetic composites led to the identification, for the silica-based sorbents, of ultrasmall iron(III) oxide nanoparticles of variable sizes depending on the pore size and surface area of the support, whilst a mixed Fe^{III}-Ti^{IV} oxide, compatible with pseudobrookite, was found in the case of the anatase support. Moreover, ^{57}Fe Mössbauer Spectroscopy and DC magnetometry were adopted also to get information on possible transformations of the Fe-bearing phases upon their application as H_2S removers from syngas and regeneration process.

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Controlled decoration of plastic surfaces with metal nanostructures

Giovanni Ferraro[a], Emiliano Fratini[a], Veronica Lucia Rossi[b], Antonio Sanesi[b], Piero Baglioni[a]

[a]Department of Chemistry ''Ugo Schiff'' & Consorzio per lo Sviluppo dei Sistemi a Grande Interfase (CSGI), University of Florence, Via della Lastruccia, 3,50019 Sesto Fiorentino, Italy[b]bioMérieux Italia Spa, Via di Campigliano, 58, 50012 Bagno a Ripoli, Florence, Italy

The controlled deposition of metal nanostructures on disposable plastic surfaces is a big challenge in different fields, as the production of optoelectronic devices and the development of solid phases for biomedical or analytical applications [1]. In the last decades, several approaches for the decoration of disposable devices with metal nanostructures were proposed. Apart from physical methods (i.e., sputtering, vapor deposition, etc.) which are suitable for flat surfaces or, in more in general, accessible substrates, the use of ligands or polymers for the binding or in-situ formation of metal nanoparticles directly on surfaces with different geometries has been reported [2-3]. For the best of our knowledge, there are no approaches for the decoration of bare plastic using already synthetized metal nanostructures.

Here, we propose the decoration of plastic substrates with metal nanostructures using an easy, maskless and industrial compatible method. Different commercial plastics (polystyrene, PS, polyethylene low density, PE-LD, polyethylene high density, PE-HD and styrene-butadiene block copolymer, SBC) were successfully decorated with citrate-capped Au nanoparticles and polyvinylpyrrolidone-capped Au nanorods. The entire process, in both cases, can be triggered and tuned by the presence of a poor solvent obtaining a controlled deposition of the metal nanostructures on the plastic surfaces. The approach was optimized in terms of incubation time and temperature, and starting concentration for the metal nanostructures dispersion thus obtaining morphologies with different degree of organization and coverage. All the prepared substrates were characterized by scanning electron microscopy and the obtained patterns were correlated with the synthesis' parameters. We believe that the principle behind this approach could be expanded to other metal nanostructures obtaining a fast and simple method for the decoration and valorization of bare plastics.

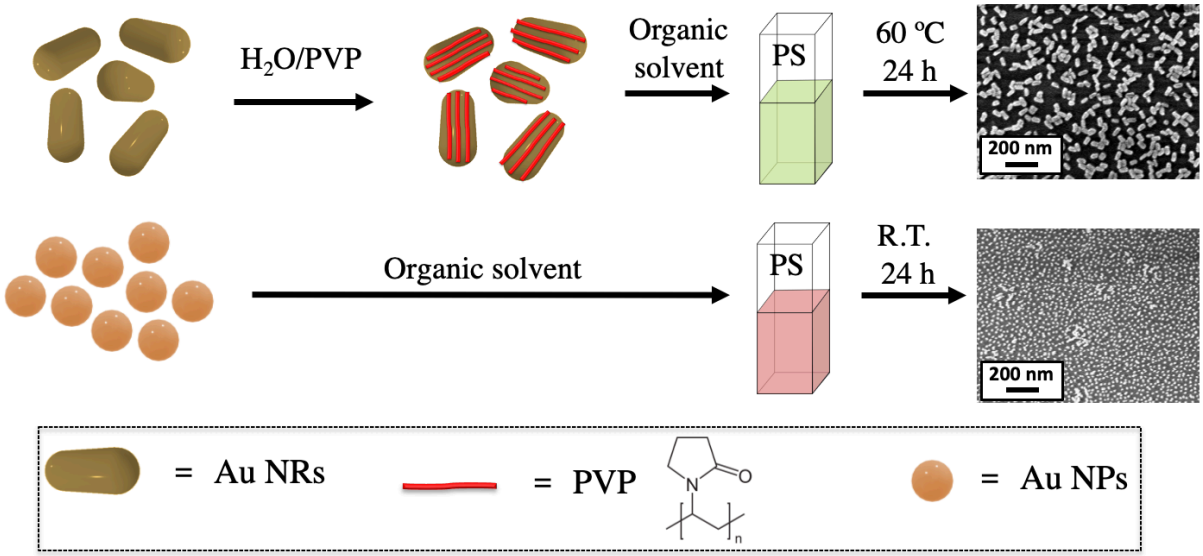

Figure. Au nanorods (Au NRs, top), and Au nanoparticles (Au NPs, bottom) synthesis and plastic decoration.

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"Distorted" self-assembly of polymer thin films at nano-curved surfaces

Roberta Ruffino [1], *Giovanni Li Destri* [1], *Nunzio Tuccitto*[1] *and Giovanni Marletta* [1]

[1]*Department of Chemical Sciences, University of Catania, Viale A. Doria 6,95125 Catania, Italy.*

The ability to control the morphology of conjugated polymer thin films in order to boost different functionalities has been the aim of many studies.[1] Fine control of the morphology and structure of the film can be obtained by exploiting the surface free energy (SFE)-induced structural effects as well as the geometric distortions induced by non-planar substrates.[2][3] In this respect, we have studied the influence of controlled nano-curvature and SFE on the self-assembly process of semicrystalline poly-3-hexylthiophene (P3HT), showing that only in the presence of an overall free energy gain, the lamellae follow the substrate morphology.[4]

In the present work, we further investigate the role played by surface energetic and geometric factors with respect to lamellae orientation on the nano-curved substrates and the related electrical properties. As to the first point, the temperature-resolved structural characterization via synchrotron radiation grazing incidence diffraction (GID), reported in Figure 1a, shows a marked variation of the crystallization temperature (Tc) with both substrate curvature and SFE. Moreover, the linear trend between structural and electrical properties of the P3HT thin films, reported in Figure 1b, reveals a linear relationship between the average orientation of P3HT lamellae, induced by the surface nanoscale curvature, and the decrease of the film electrical resistivity. Our results pave the way for new possibilities for the fine structural and functional tuning of polymeric thin films.

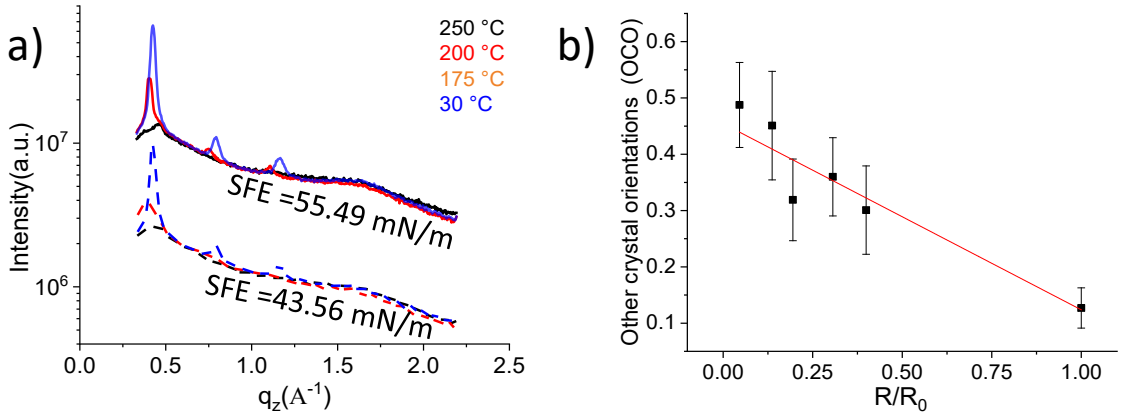

Figure 1. 1D diffraction profile, obtained during the cooling of thin films on substrates with a curvature of 0.04 cm^{-1} and different SFE (a). Linear trend between the other than perpendicular crystalline orientations and the relative electrical resistance (b). The crystalline orientations were tuned by modulating the substrate nanoscale curvature.

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Quantum Dots Enable Digital Communication Through Biological Fluids

Nunzio Tuccitto [a,b] *Federico Calì,* [a] *Luca Fichera,* [a] *Giovanni Li-Destri,* [a-b] *Grazia M. L. Messina,* [a] *Antonino Licciardello* [a,b] *and Giovanni Marletta,* [a,b]

a) Department of Chemical Sciences, Università degli Studi di Catania, Viale A. Doria 6, 95125 Catania, Italy.b) Laboratory for Molecular Surfaces and Nanotechnology-CSGI, Viale A. Doria 6, 95125 Catania, Italy

A method of communication through biological fluids will be presented. This bioinspired approach does not use electromagnetic waves but rather the exchange of chemical systems – a method known as Molecular Communication (MoCo).[1] In the report herein outlined, communication is achieved by exploiting the fluorescence properties of quantum dots which are then analysed in the domain of the Fourier transform. The problem is studied from a theoretical point of view by numerically solving the differential equation that governs the phenomenon.[2] The theoretical results are exploited to develop a prototype MoCo platform that enables the communication of infection-induced temperature variations via biological fluids to a receiver that has the task of releasing an antibiotic drug. We demonstrate that the information density transported by molecular messengers can be significantly increased by simultaneously employing and detecting messengers with discrete physico-chemical properties. Specifically, three carbon-based nanoparticles (NPs), characterized by three discrete fluorescence spectra, were employed to transmit three bits information in a single chemical pulse. Additionally, by analysing the signal Fourier transform rather than the signal itself and by employing a simple machine learning approach, it is possible to overcome any interference/artifacts caused by non-perfect synchronization between source and detector and to train a model for the recognition of the message contained in high density information NPs. Our approach is easily scalable by altering particle information or detection techniques thus demonstrating, in our opinion, that the realization and application of effective in vivo MoCo systems is drawing significantly closer.

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Plasmonic mesoporous silica coated copper sulfide nanoparticles as Near Infrared absorbing photothermal agents

Elisabetta Fanizza[a,b,], Orietta Pugliese[a], Rita Mastrogiacomo[a], Luciano De Sio[c], Alexa Guglielmelli[d], Federica Rizzi[a,b], Pierluigi Lasala[a], Maria Pia Scavo[e], Gennaro Gentile[f], Rachele Castaldo[f], Angela Agostiano[a,b], Marinella Striccoli[b], Nicoletta Depalo[b,*] and M. Lucia Curri [a,b]*

[a] Chemistry Department, University of Bari Via Orabona 4, 70126 Bari, Italy; [b] CNR-Istituto per i processi chimico-fisici, Via Orabona 4, 70126 Bari, Italy;[c] Department of Medico-Surgical Sciences and Biotechnologies, University of Rome Sapienza, Corso della Repubblica 79, 04100 Latina (LT), ITALY; [d] Department of Physics, University of Calabria, 87036, Arcavacata di Rende, Cosenza, Italy; [e] Personalized Medicine Laboratory, National Institute of Gastroenterology "S. De Bellis" Research Hospital, Via Turi 27, Castellana Grotte, Bari, Italy; [f]CNR- Institute for Polymers, Composites and Biomaterials Via Campi Flegrei 34, 80078 Pozzuoli(NA) Italy

[*]elisabetta.fanizza@uniba.it, n.depalo@ba.ipcf.cnr.it

Recently, major efforts have been devoted by translational research towards development of unconventional nanosystems for cancer diagnosis and therapy.[1] Photothermal therapy (PTT), based on conversion via photothermal transducer of light into heat represents a precise and minimally invasive modality for the treatment and management of tumors. The exploitation of the second NIR (NIR-II) light (1000−1700 nm), which penetrates deeper into tissue (approximately 3−5 cm) and has decreased photoscattering, is more suitable for deep PTT, enabling high therapeutic efficacy, deep therapeutic window, minimizing side effects.[2] Efficiency of a suitably engineered PTT agent (PTTA) depends on its stability in biological media and its ability to absorb and convert the NIR light into heat, sustaining laser irradiation without undergoing to decomposition. Many preclinical studies also demonstrate that the efficacy of PTTA is highly improved if used in combination with both radio and chemotherapeutic agents.[3]

In this regards, here organic capped plasmonic $Cu_{2-x}S$ NPs, designed in size and shape, are selected as a potential PTTA, showing a plasmon band in the NIR II region. This class of chalcogenide has been recently demonstrated active in PTT, reactive oxygen species generation, photoacoustic, magnetic resonance and positron emission tomography imagining.[1] Here, $Cu_{2-x}S$ NPs, purposely synthesized by hot injection approach [4] are encapsulated into an optically transparent hydrophilic mesoporous silica shell ($Cu_{2-x}S$@MSN), templated by surfactant, with loading and selective release capability. Different key aspects regarding structure, chemistry at the interface and property must be tackled for the achievement of an efficient photoactive heterostructures in the sub-micrometer regime. Here, core-shell $Cu_{2-x}S$@MSNs presenting a plasmon band centered at 1250 nm are synthesized and their light-to-thermal energy conversion proved by investigating the photothermal response, upon excitation with laser light at 810 nm. A temperature increase up to nearly 60°C has been attained after short-term exposure (60 sec) being the photothermal response reversible. These properties may ensure local/repeatable thermal treatment of tumor tissue with low damage to the surrounding healthy tissues, highlighting the potential of the $Cu_{2-x}S$@MSN as effective PTTA and reliable drug delivery system.

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Coating photosynthetic *Rhodobacter sphaeroides* with polydopamine

Rossella Labarile[a,b], *Danilo Vona*[a], *Gabriella Buscemi*[a,b], *Maria Varsalona*[a,b], *Matteo Grattieri*[a,b], *Angela Agostiano*[a,b], *Gianluca Maria Farinola*[a], *Massimo Trotta*[b]

[a]*Università degli Studi di Bari, Dipartimento di Chimica, Bari, Italy* [b]*CNR-IPCF Institute for Physical-Chemical Processes, Bari, Italy*

Conductive polymer layers on the surface of several bacterial species have been used to intercept and funnel outside the cells the electron flow produced by microbial metabolism and transfered them in an electric/electronic circuit of a biohybrid device.
Polydopamine (PDA), a bio-inspired polymer produced by the self-polymerization of dopamine, was selected for *Rhodobacter* (R.) *sphaeroides* coating because of its versatile adhesivity and low toxicity[1]. Furthermore, its biocompatibility allows photosynthetic organism to thrive using light and ensuring the satisfactory electronic communication[2] with the conductive surfaces, namely glassy carbon electrodes.
The coating is assembled by introducing dopamine monomers into the biological feeding medium of bacteria[3]. Electrochemical characterization was performed to investigate the electronic behavior of these biohybrids, unveiling that the polymer layer on the bacterial cells does not hinder the diffusion of the mediator and its capability to react at the electrode surface. The effects of dopamine concentration on the light-induced photoresponse of the biohybrid system will be discussed and compared to bare bacteria.

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A polyphosphoester analog of Pluronic F127 enhances the biocompatibility of monoolein-based cubosomes

Marco Fornasier,[a,b] Stefania Biffi,[c] Paolo Macor,[d] Tommy Nylander,[b] José Campos-Teràn,[b] Friedrik Wurm,[e] Sergio Murgia[f]

[a] Dept. of Chemical and Geological Sciences, University of Cagliari, Italy; [b] Dept. of Chemistry and Engineering, Lund University, Sweden; [c] Institute for Maternal and Child Health, IRCCS Burlo Garofolo, Trieste, Italy; [d] Department of Life Sciences, University of Trieste, Italy; [e] Max Planck Institute for Polymer Research, Mainz, Germany; [f] Dept. of Life and Environmental Sciences, University of Cagliari, Italy.

The strong need for biocompatible and biodegradable theranostic formulations represents a fertile research field. Among the theranostic nanocarriers studied, non-lamellar lyotropic liquid crystalline nanoparticles (LLCNPs) have been highlighted as possible alternatives to vesicles,[1] also due to the higher drug content they can encapsulate per nanoparticle. To avoid nanoparticles coalescence, non-lamellar lipid-based carriers often require a steric stabilizer, which can exert a certain degree of cytotoxicity. Moreover, the stabilizer may affect the inner structure of the nanoparticles, influencing the drug release properties.

Aiming to address these issues, we studied the applicability of a novel biodegradable polyphosphoester (PPE) analog of Pluronic F127 (PF127) as a stabilizer for monoolein-based cubosomes (nanometric aqueous dispersion of a bicontinuous cubic phase).[2]

Commonly, PF127 affects monoolein self-assembly giving a mixture of two bicontinuous cubic phases (space groups Pn3m and Im3m), due to the interactions between the hydrophobic moiety of the polymer and the lipid bilayer.[3] When PPE is used in place of poloxamer 407, only the Pn3m phase could be observed by SAXS investigations. PPE stabilized cubosomes exhibited a thermo-responsive behavior in the temperature range 25 – 50 °C, with a reversible bicontinuous cubic-to-hexagonal phase transition. The morphology and the hydrodynamic size, evaluated by cryo-TEM and DLS, are in line with the those reported in the literature for these kinds of LLCNPs stabilized by Pluronic F127 or F108.[1] The surface characterization of nanoparticles stabilized either with PPE or PF127 was conducted *via* QCM-D on both hydrophilic and hydrophobic surfaces over different biologically relevant pHs (4.5 – 7.4). The adsorption of the PPE-stabilized LLCNPs was higher on the hydrophobic surface and at acidic pHs (5 – 6), highlighting the presence of hydrophobic patches on the surface. Finally, the biocompatibility of the two (PPE- and PF127-stabilized) cubosomes formulations was investigated against two different cell lines (HUVEC and HEK) and for their hemolytic properties. It was observed that the novel formulation is less cytotoxic over the whole cubosome concentration range considered (25 – 100 μg/mL). Moreover, PPE-stabilized cubosomes showed much higher hemocompatibility with respect to PF127-stabilized cubosomes and did not activate the complement system *in vitro* in a significant manner, in comparison to cubosomes formulated with PF127.

This physico-chemical and biological characterization proved PPE as a suitable candidate for the formulation of theranostic LLCNPs.

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X-ray Scattering Scanning Microscopies – novel diagnostic tools of pathologic tissues. A focus on aneurysms, breast cancer and diabetes

Cinzia Giannini, Davide Altamura, Teresa Sibillano, Alberta Terzi, Liberato De Caro, Dritan Siliqi

Institute of Crystallography – National Research Council - Bari

X-ray Small and Wide Angle Scattering scanning microscopies have been recently employed as novel diagnostic tools to inspect morphological and structural changes - occurring at the atomic and nano scale - in pathologic tissues.
Structural changes in type 1 collagen (supra-molecular and molecular) structure have been diagnosed by means of these techniques in keratoconus [2], diabetes mellitus [2,3], coxarthrosis [4], aneurysms [5] and breast cancer [6] affected tissues.
Here we will focus on in vitro studies on aneurysms, breast cancer and diabetes.

- In *aneurysms and breast cancer*, micro-calcifications were detected, their chemical and crystallographic nature was identified, and they were co-localized with respect to type 1 collagen.
- In *diabetes*, nano-structural changes of type 1 collagen induced by extremely high doses of sugars (glucose/galactose and ribose) were detected in decellularized tissues of bovine pericardia soaked at increasing concentration (0, 2.5, 5, 10, 20 and 40 mg/mL), and incubated at 37°C for 3, 14, 30 and 90 days.

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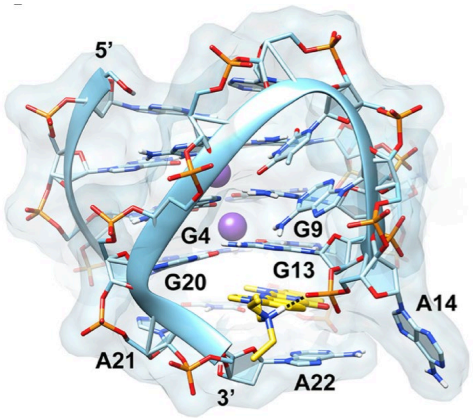
G-quadruplex within *KRAS* gene promoter: a physicochemical study

Federica D'Aria, Jussara Amato, Bruno Pagano, Concetta Giancola

Department of Pharmacy, University of Naples Federico II, Via D. Montesano 49, 80131 Naples, Italy

The structural polymorphism of DNA allows for the formation of non-canonical secondary structures, such as G-quadruplexes (G4s). G4s are found within important functional genomic regions like telomeres and gene promoters. G4s are particularly abundant in the promoters of several proto-oncogenes whose overexpression leads to cancer development, where, once stabilized, they can downregulate the gene expression. For this reason, the search for ligands able to bind and selectively stabilize specific G4s is pharmacologically very important. Thermodynamic studies of G4s stability and interaction with ligands are essential for designing and optimizing new drugs. The *KRAS* proto-oncogene encodes for the homonymous GTPase and is overexpressed in up to 95% of pancreatic ductal adenocarcinoma (PDAC) cases. Its promoter region contains guanine-rich sequences able to form G4 structures. Here, we studied the thermodynamic stability of *KRAS* promoter G4s as well as their interaction with both well-known and novel G4-targeting compounds with different molecular scaffolds [1,2]. The ability of these compounds to stabilize the G4 DNA and their selectivity for *KRAS* G4 against double helix DNA was also analyzed. The affinity constant and the binding stoichiometry of these compounds were obtained by fluorescence titration. Finally, biological experiments were also performed to evaluate the activity of some of them [2].



NMR structure of a *KRAS* G4 (PDB: 5I2V) and predicted binding pose of a ligand (yellow sticks). DNA is shown as cartoon and transparent surface. Nucleotides are highlighted as sticks. K^+ ions are depicted as purple spheres.

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Liposome/Polymer Assembly for Oral Delivery of Curcumin

V. De Leo [a], A. M. Maurelli [a], F. Ciriaco [a], S. Di Gioia [b], M. Conese [b], A. Agostiano [a], L. Catucci [a]

[a] Department of Chemistry, University of Bari, Via Orabona 4, 70126 Bari, Italy [b] Department of Medical and Surgical Sciences, University of Foggia, Foggia, Italy

Curcumin, a polyphenol isolated from Curcuma longa rhizome, exerts numerous beneficial effects on human health due to its antioxidant, anti-inflammatory, and also anticarcinogenic properties. However, curcumin shows low aqueous solubility and therefore very poor bioavailability, *in vivo* instability, and rapid metabolism. Therefore, encapsulation of curcumin in liposomes adapted for oral delivery could be a valid approach to protect it from degradation in the gastrointestinal tract (GIT) and promote its absorption. However, 1st generation vesicles are not suitable for oral delivery and suffer from some limitations including physical instability, uncontrolled release properties and low targeting ability. Coupling vesicles with polymers of various nature and through various assembly configurations is an effective strategy to overcome these limitations. This work illustrates how it is possible to adapt liposomes to oral delivery of curcumin by modulating their composition and coupling them to a suitable polymeric cover.

Nanostructure liposomes prepared by micelle-to-vesicle transition method were coated with the pH-sensitive polymer Eudragit S100 using a fast and easily scalable pH-driven method [1]. The maximum EE% obtained was around 98%. Liposomes were very stable, showing a low tendency to aggregate both at 4 ° C and 25 ° C. The antioxidant and release properties have proved excellent, with a TEAC comparable with that of free curcumin and a cumulative release complete after 200 min. TEM investigations revealed that the Eudragit S100 coating includes several liposomes into clusters of variable shape and size. Eudragit S100 coating was effective in protecting the liposomes, which retained high curcumin antioxidant activity after dissolution of the polymer shell in slightly alkaline conditions. Prepared vesicles are able to enter in Caco-2 cells through a mechanism of endocytosis where they exert a protective action against oxidative stress as proved by in vitro tests [2].

Subsequently, liposomes with a double polymer shell were prepared to gain mucus penetrating and bile salts resistant features in GIT. Vesicles were covered with a first polymer shell of PEG-2000 and then with a second shell of Eudragit-S100. *In silico* investigations have been conducted to optimize the encapsulation efficiency (EE%) and the loading capacity (LC%) of the curcumin in these conditions. The optimization is based on the application of a second-degree polynomial interpolation with two variables to the experimental data, which allowed to predict the values of lipidic and curcumin concentration in order to maximize EE% and LC%.

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Nanoantibiotics: design of multifunctional MSN nanosystems containing both antibiotic and copper ions to combat bone infection

M. Mura [a,b], B. Gonzalez [a], I. Izquierdo-Barba [a], A. Salis [b], M. Vallet-Regi [a]

[a] *Department of Chemistry in Pharmaceutical Sciences (Teaching Unit of Inorganic and Bioinorganic Chemistry) of the Faculty of Pharmacy of the Universidad Complutense de Madrid, 28040 Madrid, Spain.* [b] *Department of Chemical and Geological Sciences, University of Cagliari-CSGI, Cittadella Universitaria, 09042 Monserrato, CA.*

Finding novel strategies to combat bone infections is a major challenge for the biomedical scientific community [1]. Currently, mesoporous silica nanoparticles (MSNs) have been proposed as promising drug nanocarriers for the destruction of biofilms [2]. It has been demonstrated that polycationic macromolecules such as dendrimers grafted on MSNs surface notably increases the effectiveness of the loaded antibiotic [3,4]. Here, the design of novel multifunctional MSN-based nanosystems with high efficacy against bacterial biofilms is described. The nanosystem is composed of MSNs loaded with antibiotics, e.g. levofloxacin or rifampicin, and externally functionalized with a polypropylenimine dendrimer of third generation (G3) and copper ions. The nanosystems were characterized by XRD, TEM, EDS, TGA, DLS, ELS, FTIR and elemental analysis. The antibiotic loading and release were evaluated through UV-Vis and fluorescence spectroscopies. The polycationic dendrimer allows the binding of copper ions on the functionalized MSNs surface through their complexation by the tertiary amine groups as well as the MSNs internalization in the bacteria cells. The function of Cu^{2+} ions is to inhibit the development of bacterial resistance [5,6]. The antimicrobial activity was verified by testing the direct effect of the MSN nanosystems onto *S. aureus* biofilms. The obtained results showed a synergistic effect between the antibiotic and copper ions which is probably increased due to bacteria internalization.

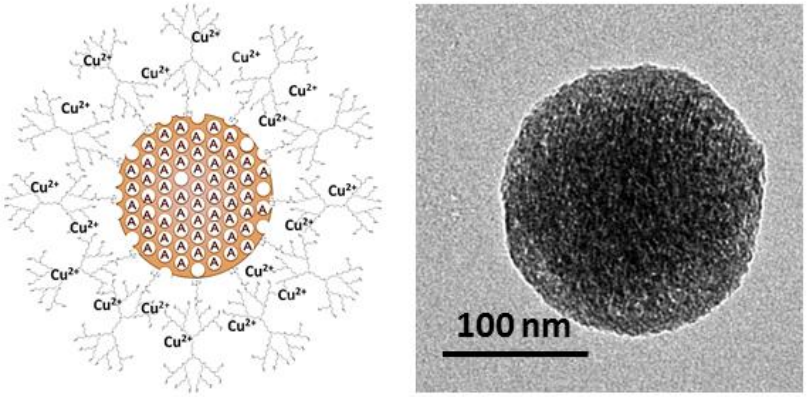

Figure 1. MSN-Antibiotic-G3-Cu^{2+} scheme and TEM image of the nanosystem.

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Crystallization of amorphous calcium phosphate to hydroxyapatite nanoparticles: new insights in the field of biomaterials and biomineralization

Lorenzo Degli Esposti[a,], Francesca Carella[a], Alessio Adamiano[a], José M. Delgado-López[b], Julietta V. Rau[c,d], Marco Fosca[c], Smilja Markovic[e], Nenad Ignjatovic[e], Vuk Uskokovic[f], Michele Iafisco[a]*

[a] Institute of Science and Technology for Ceramics (ISTEC), National Research Council (CNR), Via Granarolo 64, 48018 Faenza, Italy; [b] Department of Inorganic Chemistry, University of Granada, Av. Fuentenueva S/N, 18071 Granada, Spain; [c] Institute of Structure of Matter (ISM), National Research Council (CNR), Via del Fosso del Cavaliere 100, 00133 Rome, Italy; [d] Sechenov First Moscow State Medical University, Institute of Pharmacy, Department of Analytical, Physical and Colloid Chemistry, Trubetskaya 8, Build. 2, 119991 Moscow, Russia; [e] Institute of Technical Sciences of the Serbian Academy of Science and Arts, Knez Mihailova 35/IV, P. O. Box 377, 11000 Belgrade, Serbia; [f] TardigradeNano LLC, Irvine, CA, USA.

Amorphous calcium phosphate (ACP) nanoparticles are one of the most interesting and promising classes of nanomaterials for biomedical application. ACP is also of high biological relevance because it is the precursor of hydroxyapatite (HA) of bones and teeth. Recently we have developed a stable ACP nanomaterial functionalized with citrate ions that can also be doped with fluoride ions. We have discovered that citrate stabilizes ACP nanoparticles, making their amorphous structure steady for years in the dry state [1]. Furthermore, we have found out that citrate allows to tune specific properties of the final material by regulating the specific surface area, and that fluoride ions can be successfully delivered to tooth enamel when this material is used as a remineralizing agent in dentistry [1]. In addition, citrate is an important component of mineralized tissues accounting for ~2 wt% in bone [2]. In a first work we have investigated the mechanisms underlying the crystallization of citrate-ACP in two relevant aqueous media (ultrapure water and PBS), combining in situ (time-dependent Raman spectroscopy) and ex situ (TEM and SAED) characterization techniques [3]. Results demonstrate that citrate-ACP directly transforms to HA without involving the formation of any other intermediate calcium phosphate phase. Citrate desorption from ACP triggers the HA crystallization, which occurs through a surface-mediated process. In a second work we have first studied the thermal behaviour of citrate-ACP also doped with fluoride ions by differential thermal analysis [4]. Moreover, the physico-chemical features of the crystalline products as well as the in vitro cell response to the materials were investigated [4]. Interestingly, we have discovered that the thermal treatment of citrate-(F)ACP at 800°C yields HA or fluorapatite (FHA) as main product differently from ACP without citrate that, like most of the ACPs reported in literature, yields β-tricalcium phosphate. This was attributed to the Ca/P ratio of citrate-(F)ACP, that is similar to HA. The study of the crystalline products has revealed that all the (F)HA samples are non-cytotoxic, and retained carbonate ions in the crystal structure despite the heat treatment that should have induced decarbonation. These findings are highly relevant for gaining a better understanding in bone biomineralization process and for designing advanced biomaterials.

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Design and characterization of self-cleaning and antibacterial surfaces functionalized with nanocomposites for biosafety applications

Federica Arcidiacono[a], Elena Piacenza[a], Giuseppe Arrabito[b], Delia Francesca Chillura Martino[a], Bruno Giuseppe Pignataro[b]

[a] Department of Biological, Chemical, and Pharmaceutical Sciences and Technologies (STEBICEF), University of Palermo, Viale delle Scienze Ed.16 90128 Palermo, Italy [b] Department of Physics and Chemistry Emilio Segré, University of Palermo, Viale delle Scienze Ed.17 90128 Palermo, Italy

One of the ways to contract the Covid-19 is through contact with contaminated surfaces. Such surfaces expose people to risks that are difficult to control and they also constitute a way not only for the COVID pandemic spread but also for other infections, which originate from both virus and bacteria [1]. We aim to develop biosecurity materials that reduce the risk of contagion through inanimate surfaces. The formulation studied, either as spray or paint, would generate, upon solvent evaporation, a stable film capable of adhering to a specific surface. In this preliminary study, the films were fabricated with 1, 5, 10, 15 % w/w of zinc oxide (ZnO) nanoparticles incorporated into a polymeric matrix through a casting process. The structure and properties of the film were investigated by X-ray diffraction technique (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), UV-Visible spectroscopy, and contact angle measurement. Photocatalytic activity of ZnO was studied by monitoring the degradation of methylene blue in an aqueous suspension. In future studies, we expect to explore the biocide activity of the synthesized films through *in vitro* tests on bacteria models such as *Staphylococcus aureus* and *Escherichia coli*.

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Innovative and green synthesis of biocompatible Selenium nanoparticles in a confined environment with promising antimicrobial activity

Elena Piacenza[a], Federica Arcidiacono[a], Alessandro Presentato[a], Alessandra Del Giudice[b], Luciano Galantini[b], Delia F. Chillura Martino[a]

[a] Department of Biological, Chemical, and Pharmaceutical Sciences and Technologies (STEBICEF), University of Palermo, Viale delle Scienze Ed. 16, 90128 Palermo, Italy[b] Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro 5, 00185 Roma, Italy

Selenium nanoparticles (SeNPs) have recently gained technological interest, due to their physical-chemical versatility and high biocompatibility [1-2]. Several synthetic procedures aimed at generating structurally different, homogeneous, and stable SeNPs have been developed since the early 2000s, yet most of these methods rely on dangerous operational conditions and toxic reagents that endanger human health and the environment [1]. Thus, researchers worldwide are forced to find eco-friendly alternatives, which are mostly based on the use of biocompatible reducing agents [1]. Nevertheless, a crucial drawback of these processes is the low thermodynamic stability that the oxidized substances provide to SeNPs, causing their rapid aggregation and impairing their application.

In the present study, an innovative synthesis was designed to obtain stable and biocompatible SeNPs. This process was carried out in a confined environment constituted by sodium oleate (NaOl) micelles by using the amino acid L-cysteine as reducing agent. The resulting colloidal dispersion was stable for over a month at room temperature, thus suggesting the stabilizing role exerted by NaOl. The physical-chemical characterization (UV-Visible spectroscopy, SEM, DLS, and SAXS) of the as-obtained materials revealed the generation of spherical and small (15-25 nm) SeNPs. The colloidal stability of SeNPs impaired their transition towards nanorods (NRs), i.e., the most thermodynamically stable form of Se^0 [3]. Moreover, given the stability and biocompatibility of the SeNP@NaOl system and the amphiphilic nature of NaOl, these suspensions were used as a carrier for *Citrus* essential oil (CEO) to generate a nanoformulation featuring a synergistic antimicrobial effect. Indeed, although CEO features good antimicrobial potential even towards multidrug resistant pathogens, its efficacy is often impaired by its low bioavailability and stability, making it necessary to find strategies aimed at overcoming these practical issues [4]. Similarly, SeNPs can exert antimicrobial activity towards several bacterial strains [2] yet this action is generally explicated at high NP concentrations, potentially constituting a risk for human health. Thus, the SeNPs@NaOl@CEO nanoformulation may simultaneously attenuate these drawbacks and limit the arising of resistance mechanisms within pathogen microorganisms. As a result, *in vitro* antimicrobial assays revealed that the obtained nanoformulation acted as a biocide towards the pathogen indicator strain *Staphylococcus aureus* ATCC 25923, therefore indicating its promising potential as innovative, green, and biocompatible antimicrobial agent.

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Green synthesis of Gold nanoparticles by using grape seeds wastewater: physico-chemical characterization and investigation of their related antioxidant features for cosmetic and biomedical applications

Jennifer Gubitosa[a], *Vito Rizzi*[a], *Angela Agostiano*[a,b], *Paola Fini*[b], *Pinalysa Cosma*[a*]

[a]*Università degli Studi "Aldo Moro" di Bari, Dipartimento di Chimica, Via Orabona, 4- 70126 Bari, Italy;*[b]*Consiglio Nazionale delle Ricerche CNR-IPCF, UOS Bari, Via Orabona, 4- 70126 Bari, Italy.*

During the last decades, the demand of processes developed according to circular economy principles is progressively increasing. Among several aims, an alternative life for wastes as resources has been mainly considered as paradigm, due to the rapid industrialization and production of wastes of different typologies. For the purpose, a particular attention has been devoted towards food/agricultural wastes, as sustainable and renewable products. Indeed, many studies have been performed to propose strategies for transforming them and their by-products into value-added products. [1] Starting from these premises, a one pot green approach for the synthesis of gold nanoparticles (AuNPs) by using grape seeds wastewater has been developed during this work. [2,3] The obtained AuNPs have been characterized through several complementary techniques, namely UV-Visible, ATR-FTIR and XPS spectroscopies, XRD, TEM, DLS and Zeta Potential analyses. The role of the ionic strength, pH, and temperature after the AuNPs synthesis have been investigated for assessing if their stability could be affected by changing these physico-chemical parameters. The AuNPs photostability has been also explored at different irradiation times, by means of a sun simulator lamp. Foreseeing a potential use of the as synthesized AuNPs in cosmetic and biomedical field as multifunctional platforms, their antioxidant and skin-lightening activities have been tested by performing the ABTS and the tyrosinase-inhibition assays, respectively. [4] A preliminary *in-vitro* evaluation about the effect of AuNPs on cells viability has been also assessed, observing interesting results.

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A novel approach for the evaluation of the defect clusters content in doped ceria through *in-situ* high pressure x-ray diffraction

Cristina Artini [a,b], *Sara Massardo* [a], *Maria Maddalena Carnasciali* [a,c], *Boby Joseph* [d], *Marcella Pani* [a,e], *Maurizio Ferretti* [a]

[a] *DCCI, Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso 31, 16146 Genova, Italy;* [b] *Institute of Condensed Matter Chemistry and Technologies for Energy, National Research Council, CNR-ICMATE, Via De Marini 6, 16149 Genova, Italy;* [c] *INSTM, Genova Research Unit, Via Dodecaneso 31, 16146 Genova, Italy;* [d] *Elettra - Sincrotrone Trieste S.C.p.A., ss 14, km 163.5, 34149 Basovizza, Trieste, Italy;* [e] *CNR-SPIN Genova, Corso Perrone 24, 16152 Genova, Italy.*

Trivalent rare earth (RE)-doped ceria systems $Ce_{1-x}RE_xO_{2-x/2}$ are currently widely studied as electrolytes in solid oxide fuel and electrolysis cells operating in the intermediate temperature range (IT-SOFCs and SOECs, respectively) due to their high values of ionic conductivity between 773 and 973 K. The main drawback to their use resides in the formation of RE-based defect clusters over a certain *x*, which hinder the movement of oxygen vacancies through the structure, thus reducing ionic conductivity [1]. The nature of defects occurring in doped ceria is strictly connected to the crystallographic properties of the material. CeO_2 is characterized by a fluorite-like cubic cell (so called F) belonging to the $Fm\bar{3}m$ space group. This structure is stable even when Ce^{4+} is partly substituted by a RE^{3+} ion; in the resulting $Ce_{1-x}RE_xO_{2-x/2}$ solid solution the oxygen vacancies are free to move through the lattice, leading to the desired ionic conductivity properties. Nevertheless, above a certain RE content, superstructure peaks marking the presence of RE_2O_3 defect clusters, referable to the $Ia\bar{3}$ space group (the so called C-phase) appear in the diffraction pattern. These defect clusters have a negative impact on ionic conductivity, as they force vacancies to occupy certain fixed crystallographic sites.

The structural nature and the spatial extent of the C-based local ordering have been the subject of numerous experimental and theoretical studies [2], but in spite of the relevance of the issue, the evaluation of the defect aggregates amount, and hence the correlation with the overall oxide stoichiometry, are still open issues. In this work, a novel approach based on *in-situ* synchrotron high-pressure x-ray diffraction (HP-XRD) is proposed and applied to (Nd,Tm)-, Sm- and Lu-doped ceria, in order to provide a quantitative evaluation of the amount of C defect aggregates, and therefore of the composition of the F phase [3]. The technique relies on the exhaustive work by Anderson and Nafe [4], who analyzed a large amount of data from different oxides and proposed a relation connecting the zero-pressure atomic volume (V_{at}) and the bulk modulus (K): in particular, these authors found an empirical linear relation between lnK and $\ln(2V_{at})$. The comparison between the experimental and expected trends allows to recognize the effect of oxygen vacancies on V_{at}, which can be further used to calculate the amount of C defect aggregates. Our high-pressure diffraction data analysis reveals that defect clusters are present even at the lowest considered *x* value, and their content increases with increasing *x* and decreasing the RE^{3+} size. We could conclude that the detection limit of defects by x-ray diffraction is correlated to the defects size rather than to their amount, and that the movement of vacancies is hindered by the presence of defects, irrespective of their size and association degree.

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Super activated biochar for solid state hydrogen storage and supercapacitors preparation

C. Milanese[a], I. Frosi[a,b], A. Girella[a], S. Puoti[a], G. Magnani[c], D. Pontiroli[c,] M. Riccò[c], A. Papetti[b]*

[a] *Pavia Hydrogen Lab, C.S.G.I. & Dipartimento di Chimica, Università di Pavia, Viale Taramelli 16, I-27100, Pavia, Italy;*
[b] *Pavia FoodLab, Dipartimento di Scienze del Farmaco, Università di Pavia, Viale Taramelli 12, I-27100, Pavia, Italy;*
[c] *Nanocarbon Laboratory, DSMFI, Università di Parma, Parco Area delle Scienze 7/a, I-43124, Parma, Italy*

Recently biochar, the carbon side-product in the pyrolysis/gasification of residual waste biomasses, started to receive a widespread attention in the field of the electrical energy-storage, thanks to its hierarchical porous structure inherited from biomass precursors, its excellent chemical and electrochemical stability, high conductivity, high surface area and inexpensiveness. In particular, biochar converted to activated carbon (SSA > 1000m^2/g) through a chemical activation with KOH appears now to be a new cost-effective and environmentally-friendly carbon material with great application prospect in the field of energy-storage applications. We report here on the preparation of novel hierarchically-porous super-activated carbon materials originating from biochar derived by the pyrolysis of poultry litter (PL) and of rice bran (RB). The chemical activation process proved to be efficient to remove the majority of impurities other than carbon, stabilizing highly porous hierarchical structures with local graphene-like morphology. The porous compound obtained by PL demonstrated to behave as an excellent electrode material for high-performance symmetric supercapacitors (SCs), reaching high specific capacitance up to 230 F/g. On the contrary, the compound obtained by RB shows a very good hydrogen storage ability, adsorbing up to 3.5 wt % of hydrogen in around 20 seconds at -196°C and around 1.5 wt% at room temperature. Work is in progress to optimize the pyrolysis and activation conditions and to improve the performance of the materials by decoration with transition metals. The availability, the biocompatibility and the inexpensiveness of the starting materials suggest possible large-scale applications for such devices, for example in the field of transportation or in renewable energy-grids, but also in the field of bio-medicine.

Emissive Layered Perovskite Nanocrystals

Emanuela Sartori[a,b], Federico Locardi[a,b], Marta Campolucci[a,b], Dmitry Baranov[b], Liberato Manna[b], Zeger Hens[c], Maurizio Ferretti[a]

[a]Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy; [b]Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy; [c]PCN Research Group, Department of Chemistry, Ghent University, Krijgslaan 281, Gent, 9000, Belgium

Lead halides perovskite (LHP) $APbX_3$ ($A = CH_3NH_3^+$, Cs^+; $X = Cl^-$, Br^-, I^-) has transformed the research on solar energy conversion and semiconductors [1]. LHPs possess excellent optoelectronic properties, which are suitable for photovoltaic (PV) applications, photodetectors and light emitting diodes [2]. The LHP crystal structure is constituted by a cubic lattice formed by corner-sharing $[PbX_6]$ octahedra forming a 3D network with A^+ cations filling the cavities in between. Unfortunately, these materials suffer from two major drawbacks: the high toxicity of Pb and the degradation induced by heating, moisture and operation conditions. One of the most studied strategy to overcome these issues is the substitution of lead by a combination of a monovalent (B^+) and a trivalent (B^{3+}) metal cations, retaining the perovskite structure. The resulting compounds, called double perovskites (DPs) or elpasolites, maintain a 3D network of alternating $[B^+X_6]$ and $[B^{3+}X_6]$ corner-sharing octahedra with an overall $A_2B^+B^{3+}X_6$ stoichiometry ($X = Cl^-$, Br^-, I^-). Another promising perovskite structure is based on the substitution of B^+ with B^{2+} cation, forming a layer lattice with the general formula $A_4B^{2+}B^{3+}{}_2X_{12}$. Several compositions have been already reported in literature with interesting optoelectronic properties; in particular, $Cs_4Mn_xCd_{1-x}Bi2Cl_{12}$ has showed a red emission both in bulk [3] and as nanocolloids [4].

In this work, our recent results in the preparation of colloidal layered perovskite NCs are presented. The synthesis followed a hot-injection method where metal carboxylates are employed together with benzoyl halides (the latter used as halide precursors). $Cs_4Mn_xCd_{1-x}Sb_2Cl_{12}$ NCs were obtained with good control over the size distribution of the final product. They show a bright red emission with a maximum of photoluminescence for the theoretical composition x = 0.2. Accordingly, their interesting optical properties make them promising materials for optoelectronic applications, such as LEDs and luminescent solar concentrators.

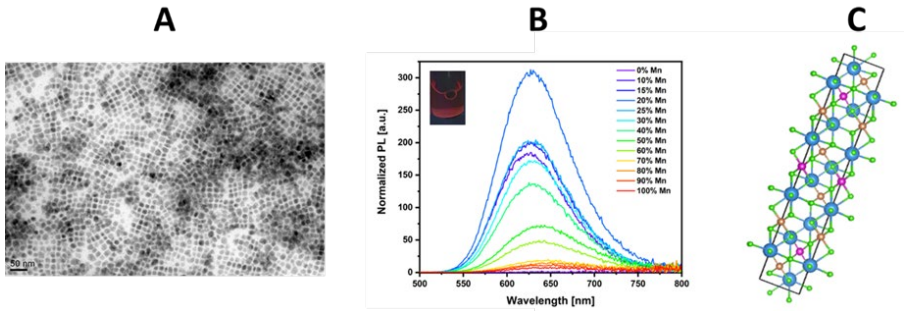

Figure. (a) TEM image and (b) photoluminescence of $Cs_4Mn_xCd_{1-x}Sb_2Cl_{12}$ NCs. (c) 2D network of $Cs_4MnSb_2Cl_{12}$ layered perovskite.

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Theoretical Description Semiconductors Interfaces: insights from DFT

Giovanni Di Liberto, Sergio Tosoni, and Gianfranco Pacchioni

Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca, Via R. Cozzi 55, 20125 Milano (MI), Italy

The essential properties owned by an efficient photocatalyst are light absorption, charge carriers separation upon excitation, and a suitable band edges positioning.[1] A growing attention is dedicated nowadays to composites, in which two or more materials are interfaced, forming a junction region that can in principle successfully address these aspects. Indeed, if the band edges are positioned according to a type-II alignement, than photogenerated electrons and holes migrate toward different sites, hindering recombination, thus promoting the desired redox processes.[2,3] Interestingly, the sign of the interface polarization, upon interfacing, can modulate the behaviour of the photocatalysts, changing their behaviour from a Type-II junction to a Direct Z-scheme one.[1] This is not a secundary aspect, since the direction of the interface polarization can determine the preferred migration paths for photo-generated electrons and holes, and its correct prediction is essential to unveil how a photocatalyst work.

Here, we present a computational overview of our recent studies on two junction photocatalysts: $BiVO_4/WO_3$ and g-C_3N_4-TiO_2, based on hybrid Density Functional Theory calculations. Besides the the nature and stability of the interface, the band edges alignment, we also predict the preferred path for carriers migration based on the analysis at the atomist level of the interface electronic properties, suggesting that, altought both systems have a type-II alignment of the band edges; $BiVO_4/WO_3$ should behave as a type-II photocatalyst,[4] and g-C_3N_4-TiO_2, as a Direct Z-Scheme one.[5] These results allow to rationalize the experimental evidence.

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Synthesis of bismuth-based hybrid perovskites for thermoelectrics

Vanira Trifiletti,[a,b] Matteo Massetti,[c] Sally Luong,[a] Simona Binetti,[b] Simone Fabiano,[c] and Oliver Fenwick [a]

[a] School of Engineering and Materials Science, Queen Mary University of London, 327 Mile End Road, London E1 4NS, UK; [b] Department of Materials Science and Solar Energy Research Center (MIB-SOLAR), University of Milano-Bicocca, Via Cozzi 55, 20125 Milano, IT; [c] Laboratory of Organic Electronics, Department of Science and Technology, Linköping University, Norrköping, SE.

Everything has a temperature, and everything making a work produce heat. Thermoelectrics, concerning the conversion between heat and electrical power, can play a crucial role in meeting the energy challenge of the future. Some industrial sites and, lately, some e-car can partially recycle the produced heat, shrinking their energy consumption. The technology exists, but it is mainly used to recover the high-temperature heat, even if most of the waste is at a temperature lower than the water boiling point, 100 °C. Therefore, in terms of planning a sustainable future, such waste heat has to be used. However, the thermoelectric generator's high price and, in some case, low efficiency limit the spread of this technology. Increase the efficiency furthermore is hard, and it is unlikely achievable with conventional compounds. Moreover, tons of active materials should be easily produced to make thermoelectric technology to be economically advantageous.
Hybrid perovskites can meet all these demands because they are cheap, and it is easy to produce nice compact thin films. They have been proposed for thermoelectric applications as they prove to have very low thermal conductivity. However, to achieve high thermoelectric performances, doping is required to enhance electrical conductivity. Here, we propose a novel synthesis for zero-dimensional methylammonium bismuth iodide $(CH_3NH_3)_3Bi_2I_9$ single crystals, thin films, and pellets. Bismuth-based hybrid perovskite has advantages over the more famous lead-based perovskite for higher stability and nontoxicity. The bismuth-based hybrid perovskites were synthesised in air and employing common and cheap solvents to keep production costs low. The synthesised materials have been characterised by UV-Vis, μ-Raman, XRD, XPS/UPS, and EDX spectroscopy measurements, and their morphology studied by SEM. Methylammonium bismuth iodide has been doped with tin and sulphur to increase the carrier concentration and mobility. The study of the fundamental properties allows us to tune the thermoelectric features. The response to thermal stimuli is providing outstanding results. The complete physicochemical characterisation of the bismuth-based hybrid perovskites designed by us will be presented, together with some preliminary results on their thermal response.

Photothermocatalytic steam reforming of methanol for H_2 production

Gian Luca Chiarello[a], Filippo Buttignol[a,b], Davide Ferri[b], Elena Selli[a]

[a] Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20132 Milano, Italy;[b] Paul Scherrer Institut, 5232 Villigen, Switzerland.

Photocatalysis may be expected to be a temperature-independent process because temperature has little effect on photon absorption. However, temperature can largely influence the dynamics of photoproduced charge carriers, also changing the mechanism and the selectivity of photocatalytic reactions. Moreover, new reaction pathways may be activated at high temperature, with synergistic or detrimental effects on photocatalysis.

In this work, the effect of temperature on the photocatalytic steam-reforming of methanol ($CH_3OH + H_2O \rightarrow CO_2 + 3\ H_2$) has been investigated in the 40-350°C temperature range with one-step flame made TiO_2 and Pt/TiO_2 [1] in a home-made stainless steel photoreactor irradiated with a 300 W Xe arc lamp. Temperature was found to strongly affect the activity of pristine TiO_2 in terms of both hydrogen production rate (r_{H2}) and selectivity towards the different by-products (CO, H_2CO and CO_2). As temperature increased up to ca. 270°C, r_{H2} increased from 3 to 27 mmol h^{-1} g_{cat}^{-1}, while no thermal activity was recorded in the dark (Fig. 1). The presence of Pt nanoparticles in Pt/TiO_2 led to an impressive increase of r_{H2} up to ca. 450 mmol h^{-1} g_{cat}^{-1} at 350°C (Fig. 1). Moreover, at temperature above 190°C the Pt/TiO_2 photocatalyst showed also a strong activity in the dark but irradiation still accounted for a ca. 20% increase of r_{H2}. At low temperature formaldehyde was the main by-product, whereas above 200°C formaldehyde could not be detected in the gas phase and CO and CO_2 became the only products of methanol oxidation with a selectivity of ca. 70% and 30%, respectively. Valuable information on the effect of temperature on the reaction mechanism under irradiation was obtained by operando Modulated Excitation DRIFT (Diffuse Reflectance Infrared Fourier Transform) analysis [2], performed by alternating irradiation and dark condition at different temperature, by *in-situ* monitoring the dynamics of reactive surface species, including water (3600-3000 cm^{-1} range), CO_2, CO adsorbed on Pt and formates.

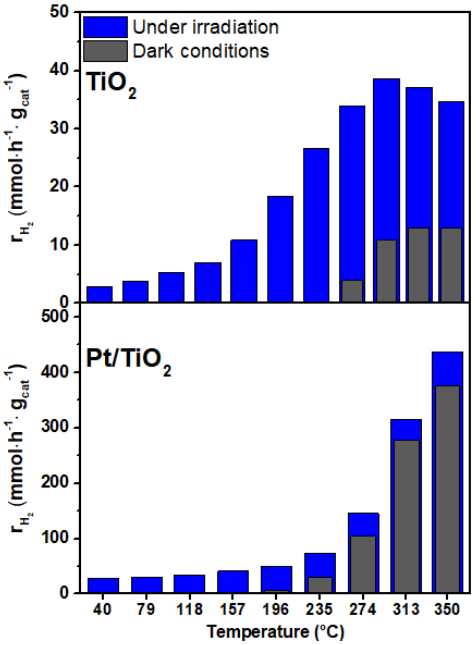

Figure 1: Effect of temperature on the H_2 production rate (r_{H2}) from methanol steam reforming under dark (grey) and UV-vis irradiation (blue) over flame-made bare TiO_2 and Pt/TiO_2.

This work demonstrated that temperature strongly affects the photocatalytic process in terms of both hydrogen production rate and by-products selectivity. The use of photoreactors combined with solar concentrators may allow the exploitation of powerful synergistic effects between photocatalytic and thermal reactions.

Acknowledgment

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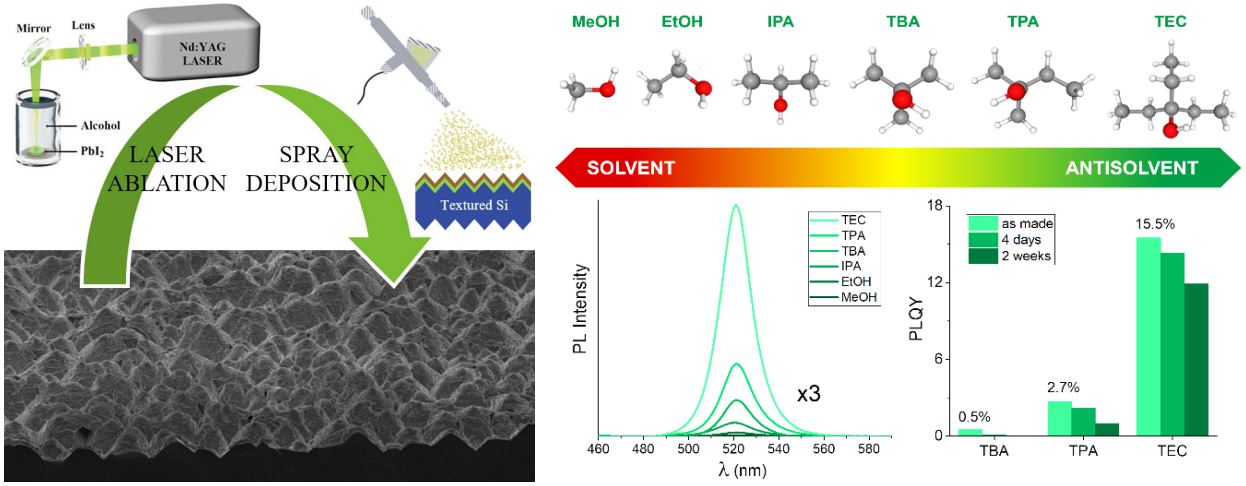
Laser ablation in solution for a more sustainable perovskite-based optoelectronics

Simone Sansoni[a], *Moreno Meneghetti*[a]

[a] *Department of Chemical Sciences, University of Padova, Via F. Marzolo 1 35131 Padova, Italy*

In the last decade, lead halide perovskite (LHP) materials have drawn enormous attention and found application in a variety of optoelectronic devices, like light-emitting diodes, solar cells, transistors, gas sensors, and photodetectors. Such a high versatility is attributable to their long carrier diffusion lengths, simple bandgap tunability, high absorption coefficients, and exceptional defect tolerance which makes solution-processing in ambient condition a viable prospect. These properties, together with the relatively low cost of perovskite precursor salts, made perovskite-based optoelectronics gaining substantial commercial appeal in the last years. The main challenges for their commercialization, are stability, scalability, and sustainability. For an effective scale-up the toxic solvents commonly used for LHPs synthesis and/or thin-films deposition must be replaced with eco-friendly ones. Recently, laser ablation in solution (LASiS) was proposed as an alternative top-down approach to synthesize LHP nanocrystals (NCs) in ambient conditions. [1] The relevant features of the nanocrystals synthesis are: (i) the presence of a graphitic/graphene phase linked to the perovskite ones, which improve their stability in ambient conditions and under electric field [2] and (ii) the possibility to completely avoid toxic solvents to obtain good-emissive LHP nanocrystals using eco-friendly alcohols. [3] By combining this methodology with a scalable deposition technique, such as spray-coating, both scalability and sustainability of perovskite-based optoelectronics has been improved. Spray-coating was also shown to be important for deposition of perovskite thin-films onto non-flat substrates, which found application in the preparation of textured silicon-perovskite tandem solar cells. [4]



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Effects of Mo^{6+} doping on the performance of $BiVO_4$ photoanodes for solar water oxidation

Annalisa Polo[a], Maria Vittoria Dozzi[a], Ivan Grigioni[a], Florent Boudoire[b], Charles R. Lhermitte[b], Kevin Sivula[b] and Elena Selli[a]

[a]Dipartimento di Chimica, Università degli Studi di Milano, Milano, Italy[b]Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

Photoelectrochemical (PEC) water splitting is a promising strategy to capture and store solar energy into hydrogen as a clean fuel. $BiVO_4$ has emerged as a leading photocatalyst for the oxygen evolution reaction (OER) despite its poor electron transport and slow water oxidation kinetics [1]. In this regard, doping $BiVO_4$ with hexavalent metal ions such as Mo^{6+} or W^{6+} has been largely employed to increase the conductivity of the material by supplying additional free electrons [2].
A preliminary study on variously Mo^{6+} doped $BiVO_4$ electrodes with dopant amounts in the 0.3–6 at.% range provided the first evidence of the positive impact of the dopant in reducing the interfacial charge transfer resistance towards water oxidation, in addition to the improved bulk conductivity resulting from the enhanced donor density upon increasing Mo^{6+} contents [3].
The major role of the Mo^{6+} dopant on the surface properties of $BiVO_4$ was then unequivocally identified by means of thorough morphological, PEC and impedance spectroscopy investigations conducted onto the pure and differently Mo^{6+} doped $BiVO_4$ photoanodes, prepared as multilayer films through spin coating deposition of aqueous precursor solutions onto FTO substrates.
An optimum 3 at.% Mo^{6+} content was identified to provide the most efficient charge carrier transport in the material bulk, resulting in a conspicuous increase in PEC performance with respect to pure $BiVO_4$ (Fig. 1). Moreover, PEC impedance spectroscopy (PEIS) analyses revealed the crucial role of Mo^{6+} in passivating surface V^{5+}/V^{4+} states acting as charge carrier traps that strongly limit the performance of pure $BiVO_4$ in water oxidation. Overall, both PEC and PEIS analyses results revealed the positive impact of Mo^{6+} dopant on the films surface-related issues, which affect the overall PEC performance of $BiVO_4$ photoanodes much more than its bulk transport properties.

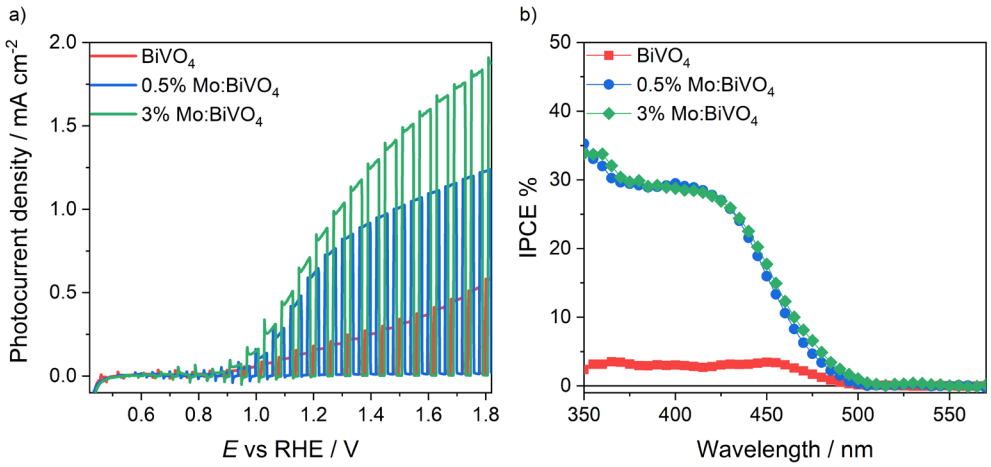

Fig. 1 *a) Linear sweep voltammetry (LSV) curves and b) incident photon to current efficiency (IPCE) plots at 1.23 V vs. RHE of the pure and Mo^{6+} doped $BiVO_4$ electrodes, in 0.5 M Na_2SO_4 electrolyte under AM 1.5 G front-side illumination.*

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Operando study of a cobalt free Li-rich layered oxide materials (LRLO) in a lithium cell

M.Tuccillo,[a] L. Silvestri,[b] S.Brutti[c]

[a]Dipartimento di Ingegneria Chimica Materiali e Ambiente, Università di Roma La Sapienza[b]Centro di Ricerca Casaccia, ENEA[c]Dipartimento di Chimica, Università di Roma La Sapienza

In the last decades, remarkable industrial and academic research efforts have been focusing on lithium-ion batteries (LIBs) for portable electronics and electric vehicles (EV)[(1)]. Generally speaking, LIBs are more expensive than other battery chemistries, but they provide the highest power and energy densities as well as longer cycle. This technology requires further development in terms of safety and performance to establish itself also in the automotive market. Thus, new materials and chemistries at the positive/negative electrode sides as well as at the electrolyte side are necessary to overcome the state-of-the-art and the commercial benchmarks. Over-stoichiometric Li-rich layered oxides (LRLO) materials are a family of promising positive electrode materials with large specific capacity and high working potential. The eco-friendly Co-free LRLOs have attracted a lot of attentions, thanks to the improved sustainability, reduced costs and outstanding performance (250 mAh g^{-1}). [(2,3)] The crystal structure and cation ordering of LRLO are a matter of controversy. In the literature the structure of these materials is identified as solid solution, with an $R\bar{3}m$ crystal structure [(4)] with partial supercell ordering of lithium ions, or as a nano-mosaic constituted of coexisting solid-solution phases with $R\bar{3}m$ and $C2/m$ structures [(5)]. Overall, extensive defectivities play a key role in the breakdown of the cation ordering in the $C2/m$ lattice that degrades in the $R\bar{3}m$ one. This structural ambiguity/instability is at the origin of the severe capacity and voltage fading in batteries originating from undesired lattice transformations. To evaluate structural evolutions during de-/lithiation, here we present a description of operando X-ray diffraction (XRD) analysis of Co-free LRLOs, during the activation and first cycle process. The experiment was conducted at the ELETTRA synchrotron at beamline MCX (Material Characterizations by X-ray Diffraction) Proposal number: 20205276.

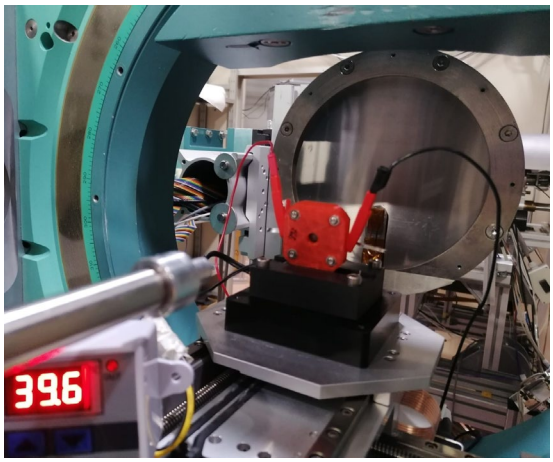

Fig. 1 Electrochemical Cell configuration using during operando experiment, obtained using a 3D printer.

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Tin-functionalized hydroxyapatite as an "ecofriendly bridge" joining water remediation and air protection processes

Sebastiano Campisi[a], Mirko Leone[a], Claudio Evangelisti[b], Georgeta Postole[c], Antonella Gervasini[a]*

[a] Dipartimento di Chimica, Università degli Studi di Milano, Via C.Golgi, 19, 20133, Milano, Italy.[b] CNR - ICCOM - Istituto di Chimica dei Composti OrganoMetallici, Via G. Moruzzi 1, I-56124 Pisa, Italy[c] Université C. Bernard Lyon 1, CNRS, IRCELYON, 2 avenue A. Einstein, F-69622, Villeurbanne, France.

Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) is a biocompatible material, that can be extracted from biowastes or synthesized from cheap precursors; it is characterized by high water insolubility ($K_{s,25°C}=2.4\cdot10^{-59}$) and high chemical and thermal stability [1]. Furthermore, its tuneable, amphoteric and highly functionalized surface allows it to permanently retain various metal ions, including Cr (III) [2]. All these features account for the ever-growing applications of HAP in the field of metal adsorption and heterogeneous catalysis. In this work both application fields were coupled in a sustainable *circular process*, whose backbone is exactly the HAP, being exploited first as sorbent for metal ions removal and then re-used as catalyst in gas-phase reactions.

Although HAP is not able to directly trap by adsorption chromate/dichromate anions, the functionalization with Sn(II) ions can give a new functionalized material able to reduce Cr(VI) ions with concurrent adsorption of the formed Cr(III), according to an *interfacial reductive adsorption process* [3]. Synthetical HAP was then functionalized by Sn(II) with different loading (2.5< Sn wt% <15) through a wet deposition procedure. Batch tests of Cr(VI) reductive adsorption (T=40°C ,$pH_i \approx$ 2 and dosage of 4.5 g/L) proved the effectiveness of Sn/HAP materials to reduce Cr(VI) and capture the Cr(III) formed. Complete Cr removal (> 99%) was observed for all the Sn/HAP samples starting from a Sn(II) concentration of 50 mg_{Sn}/g_{HAP} when contacted with a 50 ppm Cr(VI) solution. Increasing the initial Cr(VI) concentration, the effect of Sn loading became more evident. As a general trend, the maximum removal capacity increased linearly with the Sn loading on HAP up to 12.5 wt% which gave the highest removal capacity (20 mg_{Cr}/g). Kinetic profile was collected (T=40°C, [Cr(VI)]°=100 ppm) and fitted according to different empirical models; data were best described by the pseudo-second order model (PSO model), obtaining a rate constant value of $2.8\cdot10^{-3}$ g mg^{-1} min^{-1}, in agreement with values reported for other Cr(VI) reductive adsorption processes [4].

After use in Cr(VI) removal tests, samples contained Cr(III) at the surface, as confirmed by electron microscopy and X-ray Photoelectron Spectroscopy. A regeneration process is then not viable, since it should be able to reduce formed Sn(IV) to Sn(II) and simultaneously remove adsorbed Cr(III) ions at HAP surface. To overcome these issues and avoid costly disposal of the used material, a different strategy was considered, consisting in upcycling the recovered samples (Sn+Cr/HAP) into catalysts for gas phase environmental reactions in a *circular economy* perspective. Sn+Cr/HAP samples, calcined at 500°C, were then tested in a gas phase flow reaction line in catalytic reactions of environmental interest, i.e. the NH_3 Selective Catalytic reduction of NO_x (NH_3-SCR), the NH_3 Selective Catalytic Oxidation (NH_3-SCO) and catalytic oxidation of NO to NO_2. The preliminary results obtained enlightened the remarkable activity of Sn+Cr/HAP samples in catalytic oxidation processes (SCO).

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Hydrochemical study of the Turbolo basin: evaluation of the spatial and seasonal variation of surface water quality

G. A. Corrente,[a] S. Corso,[a] M. Micieli,[b,c] E. L. Argento,[b] G. Mendicino,[b] G. Botter,[c] A. Senatore,[b] A. Beneduci[a]

[a]Laboratorio di Chimica dell'Ambiente (IR SILA), Department of Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Cubo 15D, 87036 Arcavacata di Rende (CS), Italy; [b]Centro Studi per il Monitoraggio e la Modellazione Ambientale (CeSMMA), Department of Environmental Engineering, University of Calabria, Via P. Bucci, Cubo 41A, 87036 Arcavacata di Rende (CS), Italy; [c]Department of Civil, Environmental and Architectural Engineering, University of Padua, 35131 Padova, Italy.

The social and economic development of recent decades has led to a progressive deterioration in water quality, requiring decisive actions aimed at safeguarding this resource, which is often considered improperly inexhaustible. The knowledge of the qualitative characteristics of a watershed is fundamental to protect and manage it correctly. Surface water quality is controlled by both anthropogenic activities and natural factors [1]. Concerning the latter, seasonal changes in natural processes, such as temperature, precipitation, and hydrological conditions, influence water quality such that it presents different characteristics in different seasons [2]. The water quality monitoring represents an adequate approach to improve knowledge of river hydrochemistry and pollution, but it produces large data sets that require advanced statistical methods to be analysed and interpreted such as Multivariate Data Analysis [3]. The present study was carried out in the Turbolo creek basin, located in northern Calabria. The stream is a tributary of the Crati river: it originates at over 1000 m a.s.l. and flows eastward merging into the Crati river at about 75 m a.s.l., after a path of over 13 km. Water quality monitoring was based on two series of sampling, continuous and discrete. In-situ and continuous monitoring was carried out by multi-parametric probes deployed in the water stream at different locations along the basin. Discrete samples collected before, during and after some rainfall events, were also analysed ex-situ at the SILA environmental chemistry and physical chemistry-INABEC laboratories of the University of Calabria. For each sample, physical, chemical-physical and analytical parameters were determined using various methods and instrumental techniques, following the directives of the Water Framework Directive 2000/60/EC.

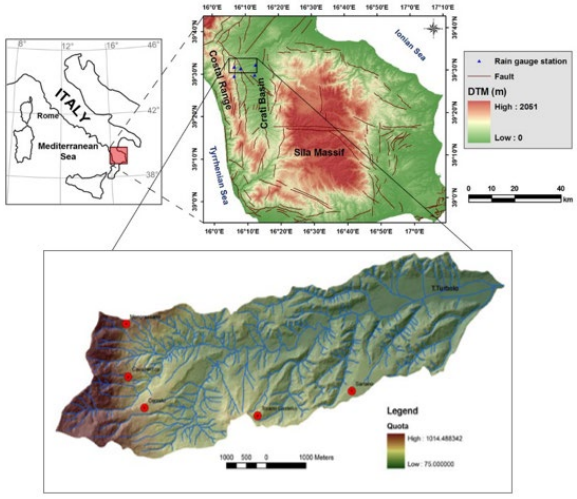

Figure 1: Area object of the study: the Turbolo basin.

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Silica Monolith for the Removal of Pollutants from Gas and Aqueous Phases

Vanessa Miglio [a], Chiara Zaccone [a], Ilaria Braschi [c] Enrico Buscaroli [b], Giovanni Golemme [c], Leonardo Marchese [a] and Chiara Bisio [a,d]

[a] Dept of Sciences and Technological Innovation, University of Eastern Piedmont, viale T. Michel 11, 15121 Alessandria. [b] Dept of Agricultural and Food Sciences, University of Bologna, viale G. Fanin 44, 40127 Bologna. [c] Dept of Environmental Engineering, University of Calabria, Via P. Bucci 45A, 87036 Rende. [d] CNR-SCITEC Istituto di Scienze e Tecnologie Chimiche "Giulio Natta", via G. Venezian 21, 20133 Milano

In recent years, chemical industries have been focusing on sustainable development approaches, promoting materials that offer performance at lower costs and reducing significantly the environmental impact. In connection to these approaches, mesoporous materials have been synthesized and extensively studied for various applications. Nevertheless, the use of powders present different handling and recycling limitations. To overcome these problems there are two possible options: (i) the preparation of pellets starting from the pre-synthesized silica powders, or (ii) the direct preparation of monoliths. Among the different types of mesoporous materials, silicas have been widely used for environmental application, since meet most of the criteria for selection of adsorbents such as high specific surface area, large pore–size and chemical inertness; for these reason, mesoporous silicas have been used for adsorption of both organic and inorganic pollutants [1]. The preparation of silica monoliths can be a convenient way to fully exploit the structural and functional properties of the material by saving, at the same time, both reactants and time, in that a single-step synthesis is required [2]. In this work, mesoporous silica monoliths have been prepared by spinodal condensation reaction [3] and then tested as adsorbents of organic pollutants from aqueous or gaseous phase. The physico-chemical features of the silica monoliths have been determined by using different experimental techniques [4]. Textural properties were found to be homogeneous over the entire length of the monolith, which has an average surface area of ca. 850 $m^2\ g^{-1}$ and a total pore volume of 1.2 $cm^3\ g^{-1}$. The monoliths were tested for the removal of toluene, chosen as a model molecule of aromatic hydrocarbons, from gas phase. A combination of FT-IR spectroscopy and volumetric analysis was adopted to study the adsorption process and gain knowledge on the interactions between adsorbent surface and toluene molecule. Silica monoliths were found to be stable to water treatment (36 h at 50 °C), even if the treatment reduced the specific surface area. Finally, the ability of the same monoliths, before and after the water treatment, to remove Rhodamine B from aqueous solution was also studied by using UV-visible spectroscopy. After water treatment, the material was able to adsorb 50% of the Rhodamine B with respect to 70% of the control sample (**Figure 1**).

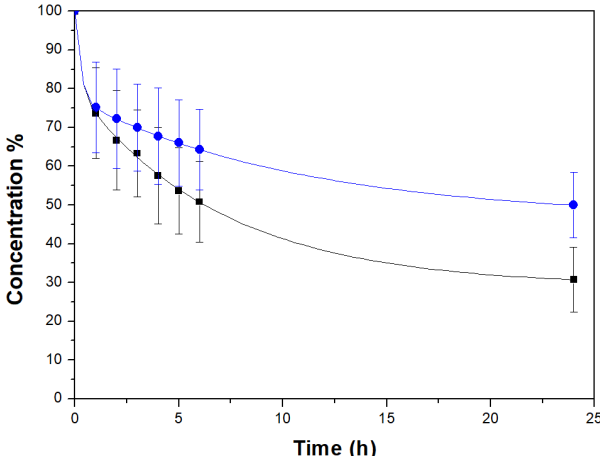

Figure 1. Concentration (%) decrease over time of $1.5x10^{-2}$ mM Rhodamine B water solution in the presence of calcined silica monolith before (■) and after water treatment (●). Error bars represent standard deviations calculated on averaging results collected from three replicated experiments.

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Investigation of mechanochemically driven CO_2 conversion over Olivine powders

G.Mulas, S.Garroni, M.A.Budroni, S.Enzo, A.Taras

Department of Chemistry and Pharmacy, University of Sassari

The development of innovative strategies aimed at mitigating the CO_2 increase in the atmosphere represents, nowadays, one of the main challenges of XXIst century, and is the object of wide interest by the scientific community [1]. Carbon Capture Utilization and Storage procedures, CCUS in the specific literature, includes several approaches and, among these, the so called "carbonation processes" of natural compounds rely on the chemical interaction of CO_2 with different classes of materials and minerals [2]. The chemical weathering of silicate mafic and ultramafic rocks, as Olivine, are an effective example of CO_2 mineralization process: silica-based minerals of Mg and Fe can react with H_2O to give H_2 and minerals of the serpentine group [$(Mg, Fe)_3Si_2O_5(OH)_4$] [3]. Moreover, in presence of CO_2, reaction condition can lead to the formation of carbonates or allow to produce CH_4 and light hydrocarbons through a Fischer-Tropsch type or Sabatier type mechanisms. However, in spite of the thermodynamically favored conditions, the reaction rate of the natural process is very slow. At the same time, the activation of such process by conventional thermal treatment requires severe conditions. Conversely, recent results suggest that the use of external mechanical energy is effective to allow a much faster reaction kinetics under mild conditions [4,5].

In such context, in the present work our attention was addressed to the study of the activation by mechanical treatment of the weathering process of Olivine in presence of H_2O and under CO_2 atmosphere. We focused either to the improvement of the reaction kinetics, either to the structural evolution of the solid phases and the CO_2 conversion to methane and light hydrocarbons.

The process was investigated under different experimental condition, and several instrumental techniques were employed in order to characterize the reactant solid systems and gaseous phases, well as to analyze the relative transformations during the chemical processes and to get complementary information concerning reaction mechanism. Structural and surface evolution was followed by resorting to X Ray Diffraction, IR and Raman spectroscopy, and SEM-EDX techniques, while Mossbauer spectroscopy allowed to gain complementary information relevant to iron oxidation states in the solid compounds. Finally, gaseous phases composition and their abundance was followed through gas chromatography analyses.

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Establishing a link between Chemistry and Complexity Science to promote Sustainability

Pier Luigi Gentili

[a] *Department of Chemistry, Biology, and Biotechnology; Università degli Studi di Perugia, Italy.*

Chemistry is living a period of change, as the same Prof. Whitesides has declared in his recent essay published in Angewandte Chemie [1]. "*We are moving from an era focused on molecules and reactions to one in which manipulations of systems of molecules and reactions will be essential parts of controlling larger systems.*" Furthermore, we are now completely aware that chemistry is at the heart of human and animal health, biological environment, and physical environment. Chemistry must embrace being a science for the benefit of society [2]. Hence, it is necessary to re-orient chemistry through Systems Thinking [3]. It is urgent to establish a strong link between Chemistry and Complexity Science [4, 5]. Complexity Science scrutinizes those Complex Systems, which are the targets of the 2030 Agenda proposed by the United Nations in 2015 [6]. Complexity Science pinpoints the features shared by all the Complex Systems; it presents effective methods for describing them. It looks for possible new principles that rule their behavior [6]. The difficulties we encounter in explaining and predicting the behavior of Complex Systems are mainly due to the Computational and Descriptive Complexities [4-6]. To overcome these difficulties, the interdisciplinary research line of Natural Computing is particularly promising [7]. Chemistry can give a solid contribution to this research line that looks for new materials and architectures to compute, new algorithms, and new models and methodologies to interpret Complex Systems by drawing inspiration from nature. I am contributing to the development of Natural Computing by mimicking some performances of the human nervous system through Systems Chemistry and Photochemistry [8-11]. Nonlinear chemical systems that work in out-of-equilibrium conditions can approach some tasks of human intelligence. They allow to developing the Chemical Artificial Intelligence [7].
This contribution will show that if we merge Chemistry and Complexity Science, we will succeed in having "One-World Chemistry," i.e., chemistry will be a science for the benefit of society and will boost the sustainable development outlined by the 2030 Agenda.

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From agricultural wastes to a resource: Kiwi Peels as recyclable adsorbent to remove emerging pollutants from water

Vito Rizzi[a], *Jennifer Gubitosa*[a], *Paola Fini*[b], *Angela Agostiano*[a,b], *Pinalysa Cosma*[a*]

[a]*Università degli Studi "Aldo Moro" di Bari, Dipartimento di Chimica, Via Orabona, 4- 70126 Bari, Italy; Consiglio Nazionale delle Ricerche CNR-IPCF, UOS Bari, Via Orabona, 4- 70126 Bari, Italy.*

Water and wastewater samples are usually polluted by several components, occurring also as a mixture of several contaminants, such as heavy metals, inorganic salts, textiles dyes, restituting a high toxicity [1]; so, suitable strategies to obtain clean water have been carefully developed, and well described in the recent and past literature. [1,2] However, as a relative emerging and worldwide problem, there is the increasing presence of Emerging Contaminants (ECs): not regulated substances that could affect both human health, and the whole environment, causing severe problems. [1,2] The adsorption process, due to the usually associated low-costs and simplicity, is largely employed to treat water. About this concern, in the last decades, the use of Peels as food/agricultural wastes have attained interest, as adsorbents, avoiding their disposal, according to the principles of Green Chemistry and Sustainable Development. [3] For the purpose, this work proposes the use of Kiwi Peels to remove emerging pollutants from water. Kiwi Peels were characterized by using in synergy FTIR-ATR, TG and SEM analyses, before and after their use, and as result they are proposed as recyclable adsorbent. In particular, after the comparison of different agricultural/food wastes, Kiwi Peels were selected, and, among the tested 14 emerging pollutants, 6 of them were successfully removed, also if present in mixtures, calculating the Kiwi Peels maximum adsorption capacities. To infer information about the behavior of Kiwi Peels during water treatments, Ciprofloxacin, a well-known and largely used antibiotic, was selected as model dangerous contaminant. The roles of ionic strength, pH values, adsorbent/pollutant amounts, and temperature values during the adsorption process were assessed giving physical and chemical information of the whole adsorption process. Furthermore, the thermodynamic, the adsorption isotherms and kinetics were studied. The Freundlich model, with a good correlation, well described the obtained results, indicating the heterogenous character of the Ciprofloxacin adsorption, with the formation of a multilayer of pollutant onto the adsorbent surface. If in the range of temperatures 283-303K, the Ciprofloxacin adsorption was favored by increasing the temperature; on the other hand, the adsorption was hindered by the further increase of temperature, due to the pollutant desorption. Both the pseudo first and second order kinetic equations seemed to describe the process with the applicability of the Weber-Morris model. By changing the pH values and ionic strength of solutions containing Ciprofloxacin, the results suggested the main presence of electrostatic interaction between the pollutant and adsorbent. In order to extend the lifetime of Kiwi Peels, desorption experiments were obtained by using hot water or 0.1 M $MgCl_2$. Despite the relatively low Kiwi Peels adsorption capacity (4 mg/g) for Ciprofloxacin, 10 cycles of adsorption/desorption were studied, evidencing the recycling of both the pollutant and Kiwi Peels.

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Use of Food Substances as chemical additives in the industrial field

Paolino Caputo [a*], Abraham A. Abe a, Cesare Oliviero Rossi a, Maria Penelote De Santo[b], Nicolas Godbert[c], Iolinda Aiello [c,d]

[a]Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, 87036 Arcavacata di Rende (CS), Italy; abraham.abe@unical.it (A.A.A.); cesare.oliviero@unical.it (C.O.R.) and paolino.caputo@unical.it (P.C.) [b] Dipartimento di Fisica e CNR-Nanotec, Università della Calabria, via Bucci 31C, 87036 Rende (CS), Italy; maria.desanto@fis.unical.it (M.P.D.); [c] MAT-InLAB, LASCAMM CR-INSTM, Unità INSTM della Calabria, Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Ponte Pietro Bucci Cubo 14C, 87036 Arcavacata di Rende (CS), Italy; nicolas.godbert@unical.it (N.G.); iolinda.aiello@unical.it (I.A.) [d] CNR NANOTEC-Istituto di Nanotecnologia U.O.S. Cosenza, 87036 Arcavacata di Rende (CS), Italy

*Speaker: paolino.caputo@unical.it

Abstract

The industrial sector, in a bid to reduce environmental pollution and the risks associated with industrial operations, is continually searching for chemical additives which are eco-compatible and are not dangerous to human health. In this body of work, we thought to use commonly used products such as cooking spices which improve the taste of food that we eat on a daily basis as additives for industrial processes. According to scientific investigation based on the molecular structure of such products, Turmeric and Curcumin – food substances which can take on the role of potential additives and can be used in the field of road pavements have been identified.

In general, adhesion promoters, anti-oxidant agents and rheological modifiers are the main and most common additives used in the asphalt industry to improve the performance of road pavements and increase their lifespan. Adhesion promoters increase the affinity between the stone aggregates and the asphalt binder (bitumen), anti-oxidant agents reduce the effects of aging which results from oxidation caused by exposure to air, water and some harsh conditions to which the road pavement is exposed while rheological modifiers increase physico-chemical properties such as the transition temperature of the binder. This research tests the effectiveness of food grade bio-additives on these three aforementioned properties. This works also seeks to hypothesize the mechanisms through which the additives confer these sought-after features on bitumen binder. This study presents the evaluation of the effects of food-based additives Turmeric and Curcumin on bitumen. Techniques such as Dynamic Shear Rheology (DSR), Atomic Force Microscopy (AFM), Nuclear Magnetic Resonance (NMR) diffusiometry, Scanning Electron Microscopy (SEM) and Boiling Test Analysis.

Environmentally friendly ZnO/Castor oil polyurethane composites for the efficient gas-phase adsorption of acetic acid

Alessio Zuliani[a], *Damiano Bandelli*,[a] *David Chelazzi*,[a] *Rodorico Giorgi*,[a] *Piero Baglioni*[a]

[a] Consorzio Interuniversatario per lo Sviluppo dei Sistemi a Grande Interfase, Firenze, Tuscany, Italy.

The development of affordable VOCs adsorption materials having low environmental impact and high VOCs adsorption capacities is still an open challenge. Herein, a novel organic-inorganic composite system for the removal of acetic acid, made of zinc oxide supported and incorporated on a polyurethane derived from castor oil is described. According to the literature, a similar approach of designing an environmentally friendly compact hybrid organo-inorganic system for the efficient and stable adsorption/absorption of acetic acid hasn't been reported yet. A biomass-derived castor oil polyurethane made of castor oil and poly(hexamethylene diisocyanate) was employed as sustainable polymer having acetic acid absorption properties, while low toxic and cheap ZnO was employed as acetic acid remover through the formation of zinc acetate. The synthesis of ZnO/COPs was proved to be environmentally friendly basing on different green metrics and easily scalabe up (up to kg-scale). A sequence of ZnO-castor oil polyurethane composite systems (denoted ZnO/COPs, where COPs stays for "Castor Oil Polyurethane") was thus prepared using three types of ZnO powders, having different particles size distributions, ranging from 20 nm to 44 µm and different commercial availabilities. The adsorption capacities of ZnO/COPs were studied by carrying out adsorption tests in small sealed chambers in saturated atmosphere of acetic acid (AA) followed by desorption under vacuum. In addition, the adsorption capacities of ZnO/COPs were investigated in 54 L glass reactors at low (ppmv scale) concentration of AA and in a 630 L wooden box naturally releasing acetic acid. The novel materials were fully characterized by infrared spectroscopy, thermogravimetric analysis and SEM images before and after the adsorption tests. The adsorption capacities obtained in the test in saturated atmosphere of AA demonstrated that ZnO/COPs could adsorb up to 0.75 g of AA per g of material while commonly employed activated charcoal could adsorb 0.2 g of AA per g of material. Best ZnO/COP sample could break down 97% of AA concentration when exposed to a ppmv starting concentration of the pollutant (in the 54 L reactors) while it could halve the AA concentration in the 630 L wooden case. The results also demonstrated a synergistic effect between the polyurethane structure and ZnO for the adsorption of AA.

Synthesis and Enhanced Capture Properties of a New BioMOF@SWCNT-BP: Recovery of the Endangered Rare Earth-Elements from Aqueous Systems

Antonio Tursi[a], Teresa F. Mastropietro[a], Rosaria Bruno[a], Mariafrancesca Baratta[a], Jesus Ferrando-Soria[b], Alexander I. Mashin[c], Fiore P. Nicoletta[a], Emilio Pardo[b], Giovanni De Filpo[a], Donatella Armentano[a]

[a]*Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, 87036, Rende, Italy;* [b]*Departamento de Química Inorgánica, Instituto de Ciencia Molecular (ICMOL), Universidad de Valencia, 46980 Paterna, Valencia, Spain;* [c] *Applied Physics and Microelectronics, Lobachevsky State University of Nizhni Novgorod, Russian Federation*

Human society is facing – among other environmental threats – an enormous challenge due to human activities. The extensive use of high-tech devices and electronics equipment in our daily life makes, among others, Rare Earth Elements (REEs) recovery from secondary sources highly required. Indeed, in the last years, the demand for raw materials such as REEs has experienced an exponential increase due to their indispensable uses in circuits of modern cutting-edge technology. For that reason, REEs are attracting attention to legislators and scientists to develop novel recovery technologies for recovering non-recycled waste materials that can end up in surface waters and ocean, thus being a source of relevant contamination for aquatic environments.
In this work, we present a novel bioMOF-based single-walled carbon nanotube buckypaper (SWCNT-BP) as a new and performant composite material (BioMOF@SWCNT-BP) for lanthanides recovery from water. The flexible and highly crystalline MOF, prepared from the natural amino acid L-threonine [1], has been homogeneously dispersed within the tangled net of a self-standing SWCNT-BP [2]. This MOF-carbon-based membrane exhibits high efficiency in both static and dynamic regimes in the recovery of lanthanides from aqueous streams outperforming the state-of-the-art materials. The known capture performances of BPs are successfully improved after incorporation of such MOF featuring hexagonal functional channels decorated with the threonine amino acid residues, which unambiguously boosted the capture properties of the final membrane, providing the appropriate adaptable functional environment to interact with lanthanides. This material's preparation presents also a potential for large-scale applications with a great potential benefit on natural aquatic ecosystems as well, considering that REEs in non-recycled waste materials may end up in surface waters and ocean.

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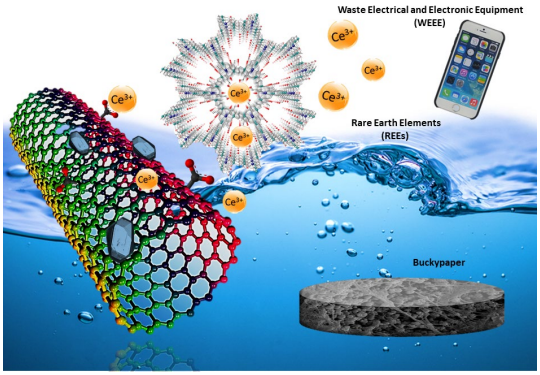
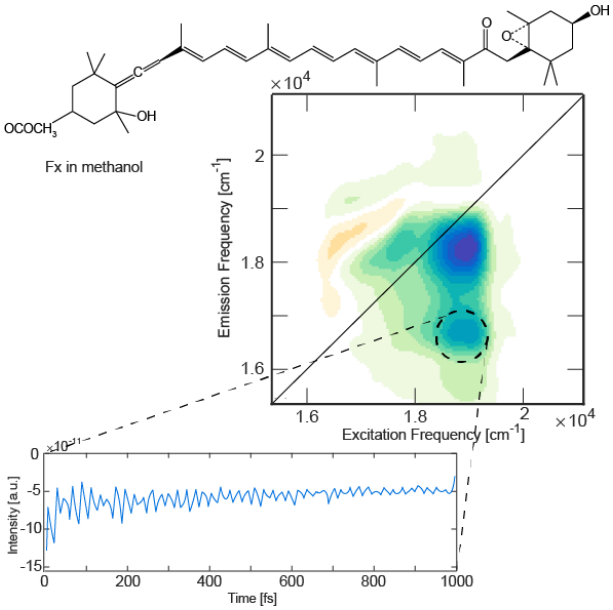


Solvent-dependent Characterization of Fucoxanthin through 2D Electronic Spectroscopy Reveals New Details on the Intramolecular Charge Transfer State Dynamics

Giampaolo Marcolin [a], Elisabetta Collini [a]

[a] *University of Padua, Department of Chemical Sciences, Padova, Italy.*



The electronic state manifolds of carotenoids and their relaxation dynamics are the object of intense investigation because most of the subtle details regulating their photophysics are still unknown. In order to contribute to this quest, here we present a solvent-dependent 2D Electronic Spectroscopy (2DES) characterization of fucoxanthin, a carbonyl carotenoid involved in the light-harvesting process of brown algae. The 2DES technique allows probing its ultrafast relaxation dynamics in the first 1000 fs after photoexcitation with a 10 fs time resolution. The obtained results help shed light on the dynamics of the first electronic state manifold and in particular on an intramolecular charge transfer state (ICT), whose photophysical properties are particularly elusive given its (almost) dark nature.[1]

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Multiple prompt and long-lived emissions from solid state purely organic materials

Alessandra Forni,[a] Chiara Botta,[a] Lucia Carlucci,[b] Clelia Giannini,[b] Elena Lucenti,[a] Daniele Malpicci,[ab] Daniele Marinotto,[a] Pierluigi Mercandelli,[b] Elena Cariati[ab]

[a] CNR-SCITEC, Istituto di Scienze e Tecnologie Chimiche "Giulio Natta", Milano, Italy; [b] Dipartimento di Chimica, Università degli Studi di Milano, Milano, Italy

Room temperature phosphorescence from purely organic materials in solid state represents a flourishing research field owing to the advantages they offer with respect to conventional metal complexes, including long afterglow lifetimes (in some cases even of few seconds), the versatility of molecular design and engineering together with excellent biocompatibility. Recently, we have reported about the rich photophysical behavior of triimidazo[1,2-*a*:1',2'-*c*:1",2"-*e*][1,3,5]triazine or cyclic triimidazole (**TT**), comprising crystallization induced emission and ultralong phosphorescence (τ up to 1 s at room temperature), associated with the formation of H aggregates through face to face strong π–π interactions in the crystal structure [1].

The introduction of one or multiple halogen atoms on the **TT** scaffold greatly modifies both its molecular and solid-state photophysical properties resulting in a complex photoluminescence with emissions going from dual fluorescence to molecular phosphorescence and supramolecular room temperature phosphorescence [2-3]. A step forward has been accomplished by the introduction of chromophoric substituents such as pyridine (**TT-Py**, see Figure 1) [4], pyrene and carbazole, all of them crystallizing in different polymorphs. The effects of these substituents on the emissive features of **TT** will be here discussed based on the results obtained from X-ray diffraction studies and DFT/TDDFT calculations.

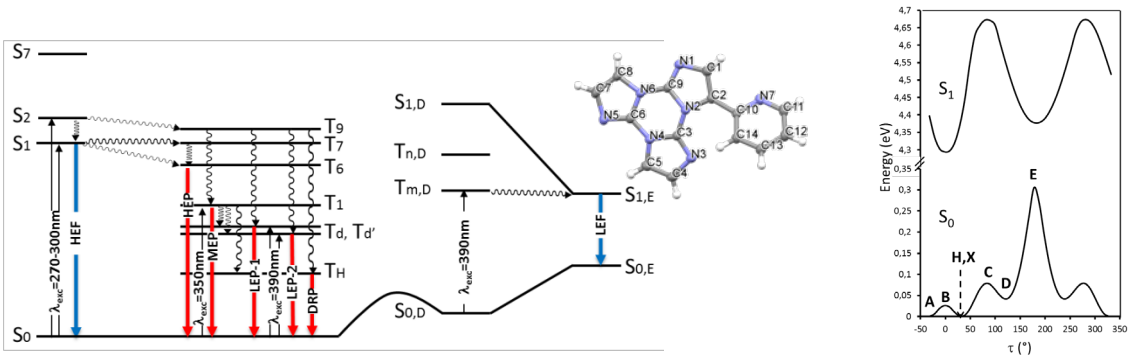

Figure 1. Left: Schematic photophysical processes of **TT-Py** (fluorescences and phosphorescences shown as blue and red arrows, respectively). Right: Scan of the relaxed potential energy surface of the S_1 and S_0 states of **TT-Py** along the N7-C10-C2-C1 torsion angle, τ, at the (TD)-ωB97X/6-311++G(d,p) level of theory. Energies are relative to the S_0 state equilibrium geometry. **A**, **H** and **X** refer to the optimized molecular structures of polymorphs **TT-Py-A**, **-H**, and **-X**, respectively. **B**, **C**, **D** and **E** denote the other stationary states.

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NMR in chiral partially ordered media: a tool for achieving conformational traits of small flexible enantiomers in solution

Salvino, R.A. [a,b]*; Celebre, G.* [a]*; Aroulanda, C.* [b]*; De Luca, G.* [a]*;*

[a] *Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Arcavacata di Rende, Cosenza, Italy;* [b] *Equipe de RMN en milieu orienté, ICMMO, UMR 8182, Université Paris-Sud, Orsay, France*

The structural and conformational determination of flexible molecules in solution is one of the most unsolved problem in modern molecular analysis. It becomes even more challenging in the case of bioactive molecules because the spatial arrangement they adopt strongly affects the interactions with ligands and their biological activity in general. The use of NMR spectroscopy combined with weakly aligning solvent has proven to be a reliable and effective method for the structural and conformational study of flexible bioactive molecules [1]. In such media, the reorientation motion of the solutes is no longer isotropic and the anisotropic interactions become measurable. However, since the alignment of the solutes is weak, simple and informative NMR spectra originate, in which the residual dipolar couplings (RDCs) are comparable to the scalar couplings and are directly observed as an additional contribution to the line splitting. Thanks to their long-range nature the RDSc allow us to determine the solute 3D structure. Indeed, by combining these experimental parameters with a robust suitable theoretical model, an accurate description of the conformational distribution in solution can be obtained [1,2]. During the years, the conformational analysis of several flexible non-steroidal anti-inflammatory drugs, belonging to the class of salicylates and α-arylpropionic acids (profens), have been performed. In these studies, a racemic mixture or a single enantiomer was considered[1,3,4], but the methodology was never applied to a pair of enantiomers to investigate their individual conformations and to understand the different solute-solvent interactions that the two enantiomers R and S form in a chiral solvent. With the purpose of undertaking this type of investigation, we report in this contribution an NMR study conduct on two couples of enantiomers dissolved in the weakly aligning solvent composed by the chiral phase of poly-γ-benzyl-L-glutamate (PBLG) and $CDCl_3$. We started by considering the simplest case consisting of the R and S enantiomers of the 4-Fluoro-α-methylbenzyl alcohol (4FMBOH) molecule, a single rotor, then moving on to the two enantiomers of the more complex molecule of 2-(5-benzoylthiophen-2-yl)propanoic acid (tiaprofenic acid), with a larger number of internal torsions. For each molecule, two different sets of RDC's were extracted, one for the R-enantiomer and one for the S-enantiomer, from 1D and 2D experiments; the combination of these experimental parameters with the theoretical approach Additive Potential-Direct probability Description (AP-DPD) [1,3,4], allowed us to obtain accurate descriptions of the probability distributions and to calculate the order parameters of each individual enantiomers.

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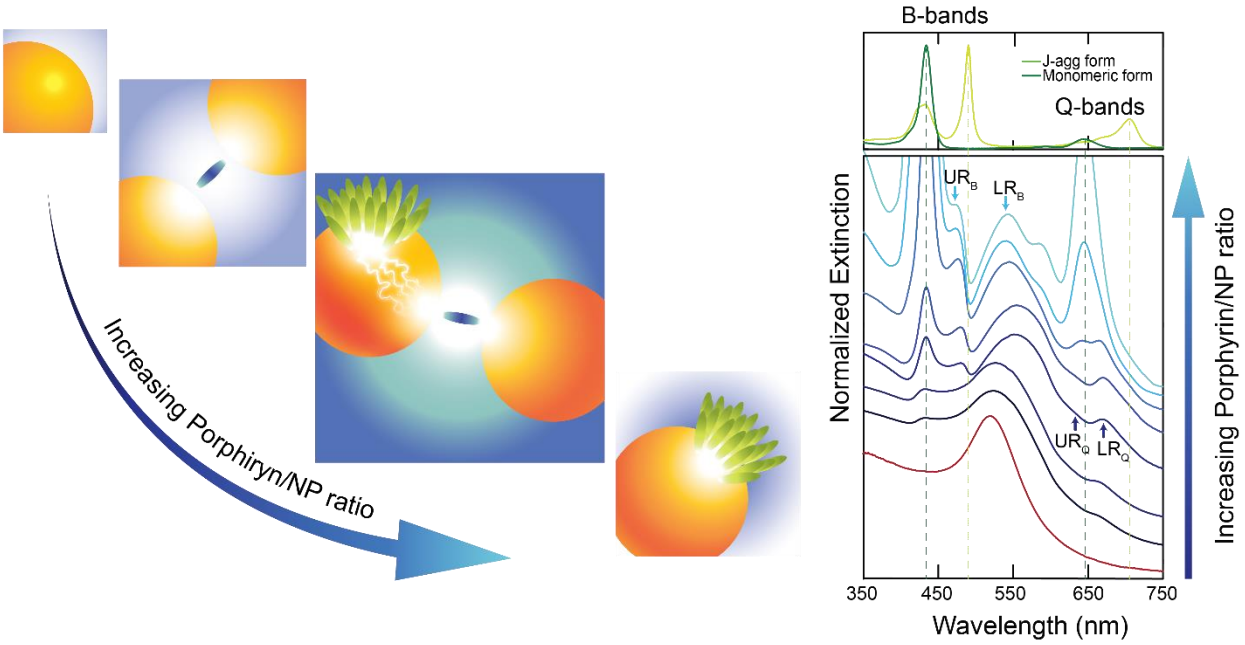
Selective Switching of Multiple Plexcitons in Colloidal Materials: Directing the Energy Flow at the Nanoscale

A. Nicola Peruffo[a], *B. Gabriel Gil*,[a]† *C. Stefano Corni*[a,b], *D. Fabrizio Mancin*[a], *E. Elisabetta Collini*[a].

Department of Chemical Sciences, University of Padova, Padova, Italy; [b]CNR Institute of Nanoscience, Modena, Italy; † present address: Institute of Cybernetics, Mathematics and Physics (ICIMAF), La Habana, Cuba



The burgeoning field of the strong light-matter coupling has long been investigated to control light at nanometer scale, and it is opening new perspectives for solar cells, quantum technologies and nanophotonics.[1] The choice of different couplings and, accordingly, different photophysical behaviors, can be governed by the various combinations of excitonic materials and plasmonic substrates, as well as the spatial arrangement of the individual components. This, in turn, leads to the formation of plexcitonic resonances, when intermediate or strong coupling is achieved. In this oral, I will present a responsive nanosystem (left image), prepared by colloidal assembly methods, where two sets of plexcitonic resonances in different coupling regimes (UR_B/LR_B and UR_Q/LR_Q in the right image) can be selectively switched on and off, acting on external conditions such as concentration and presence of anions. The two sets of plexciton resonances are built exploiting the strong coupling between cationic gold nanoparticles and the same molecular moiety, an anionic porphyrin, in different aggregation states. When both plexciton resonances are simultaneously activated in the system, evidence for a plexciton relaxation cascade has been found static fluorescence and ultrafast spectroscopy experiments. These findings have fundamental implications for achieving control over energy flow at the nanoscale.[2]

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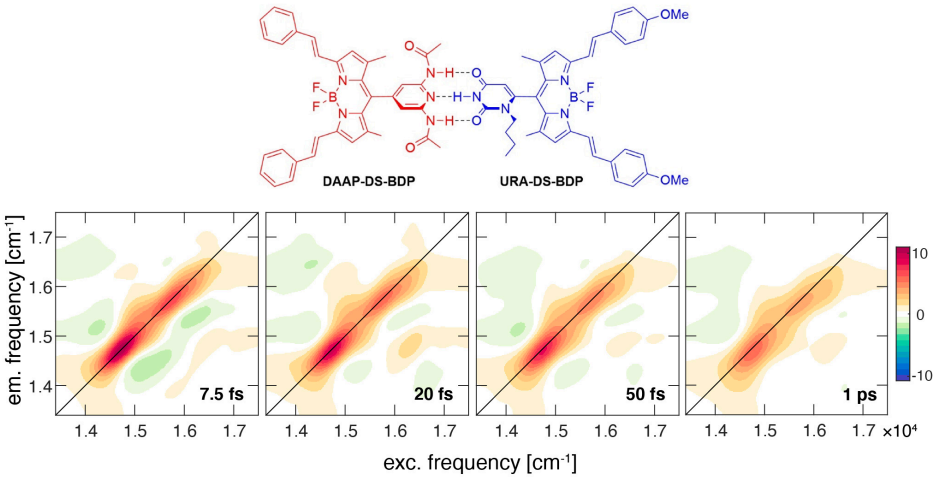
The effect of hydrogen bonds on the ultrafast relaxation dynamics of a BODIPY dimer

*Elisa Fresch,[a] Nicola Peruffo,[a] Mariachiara Trapani,[b] Massimiliano Cordaro,[c] Giovanni Bella,[c] Maria Angela Castriciano,[b] and Elisabetta Collini[a] **

[a]*Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova, Italy*[b] *CNR-ISMN, Istituto per lo Studio dei Materiali Nanostrutturati, c/o Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, V.le F. Stagno D'Alcontres 31, 98166 Messina, Italy* [c] *Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università di Messina, V.le F. Stagno D'Alcontres 31, 98166 Messina, Italy*

The influence of hydrogen bonds (H-bonds) in the structure, dynamics, and functionality of biological and artificial complex systems is the subject of intense investigation.[1] In this broad context, particular attention has recently been focused on the ultrafast H-bond dependent dynamical properties in the electronic excited state because of their potentially dramatic consequences on the mechanism, dynamics, and efficiency of photochemical reactions and photophysical processes of crucial importance for life and technology [2]. Excited-state H-bond dynamics generally occur on ultrafast time scales of hundreds of femtoseconds or less, making the characterization of associated mechanisms particularly challenging with conventional time-resolved techniques. In this work, 2D electronic spectroscopy is exploited to shed light on this still largely unexplored dynamic mechanism. An H-bonded molecular dimer prepared by self-assembly of two boron-dipyrromethene dyes has been specifically designed and synthesized for this aim. The obtained results confirm that upon formation of H-bonds and the dimer, a new ultrafast relaxation channel is activated in the ultrafast dynamics, mediated by the vibrational motions of the hydrogen donor and acceptor groups. This relaxation channel also involves, beyond intra-molecular relaxations, an inter-molecular transfer process. This is particularly significant considering the long distance between the centers of mass of the two molecules. These findings suggest that the design of H-bonded structures is a particularly powerful tool to drive the ultrafast dynamics in complex materials. [3]



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Structure and dynamics of "cool" organic pigments by solid state NMR

Francesca Martini,[a,b] Silvia Borsacchi,[b,c] Andrea Pucci,[a,b] Fabio Bellina,[a,b] Marco Lessi,[a,b] Giacomo Ruggeri,[a] Giovanni Barcaro,[d] Susanna Monti,[c] Marco Geppi[a,b]

[a]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56124 Pisa, Italy; [b]Centro per l'Integrazione della Strumentazione Scientifica dell'Università di Pisa, 56126 Pisa, Italy; [c]Istituto di Chimica dei Composti Organo Metallici, Consiglio Nazionale delle Ricerche, 56124 Pisa, Italy; [d]Istituto per i Processi Chimico-Fisici, Consiglio Nazionale delle Ricerche, 56124 Pisa, Italy

The warming of densely populated urban regions compared to the surrounding rural zones, known as Urban Heat Island (UHI) effect, is an urgent environmental issue having a tremendous impact on human health and causing a sharp raise of energy demand in city areas [1]. An available strategy to mitigate the UHI phenomenon is painting building roofs and façades with coatings containing "cool" pigments [2]. These mimic the transparent and reflective properties of certain green plants towards the near infrared (NIR) radiation, which is the main responsible for the warming of surfaces under sunlight exposure. Recently, perylene bis-imide derivatives (PBIs) have attracted a considerable interest as "cool" organic pigments [3], representing a more versatile, green and lower-cost alternative to the currently used inorganic pigments based on rare-earth oxides. However, PBIs performances are still inferior to those of inorganic compounds and further research is needed to shed light onto the complex structure-properties relationships at the basis of their optical behavior. Indeed, NIR reflectance and transparency of PBIs were found to be strongly related to the nature and position of the substituents at the PBI core. Supramolecular packing, crystallinity and particle size also play a role, but a full comprehension is still far from being achieved [3,4].

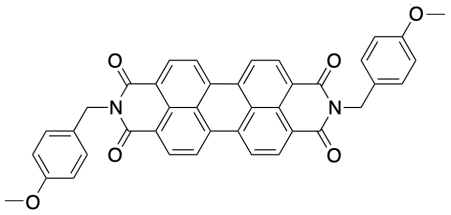

Figure 1. Structure of P-black

Solid state NMR spectroscopy (SSNMR) can be very helpful to disclose information on molecular and supramolecular features of PBIs structure, complementary to those achievable by other techniques such as X-ray diffraction (XRD) and electron microscopies. In this work SSNMR has been used in combination with density functional theory (DFT) calculations to investigate the structural and dynamic properties of the PBI pigment Paliogen Black L0086 (P-black) (Figure 1) [5], which has shown promising "cooling" properties in acrylic coatings [4,6]. The comparison with DFT predictions permitted the full assignment of the ^{13}C SSNMR spectrum, pointing out correlations between ^{13}C isotropic chemical shifts and supramolecular packing. Moreover, variable temperature ^{13}C experiments provided information on the π-flip motion involving the methoxybenzyl substituents bonded to the imide nitrogen atoms, which was found to depend on structural order as well as on the length of the alkyl linker between the substituent and the PBI core. Finally, a preliminary investigation on PBI pigments similar to P-black has been carried out, which highlighted the utility of ^{13}C SSNMR for the characterization of PBIs, especially when single-crystal XRD cannot be applied.

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Bidimensional black Phosphorus: surface functionalization, heterostructures with organic molecules, applications

Margherita Bolognesi,[a] Salvatore Moschetto,[a] Marco Brucale,[a] Gabriele Manca,[b] Luana Persano,[c] Mariangela Castriciano,[d] Peter Beton,[e] Maurizio Peruzzini,[b] Stefano Toffanin [a]

[a] *Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), Consiglio Nazionale delle Ricerche (CNR), Via P. Gobetti 101, 40129 Bologna, Italy*
[b] *Istituto di Chimica dei Composti Organometallici (ICCOM), Consiglio Nazionale delle Ricerche (CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Florence, Italy*
[c] *Laboratorio NEST, Scuola Normale Superiore and Istituto Nanoscienze, Consiglio Nazionale delle Ricerche (CNR), Piazza San Silvestro 12, I-56127 Pisa, Italy*
[d] *Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), Consiglio Nazionale delle Ricerche (CNR), c/o Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali, University of Messina, V.le F. Stagno d'Alcontres 31, 98166 Messina, Italy*
[e] *School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, UK*

Semiconducting two dimensional black phosphorus (2D bP) has recently attracted a lot of interest thanks to its peculiar properties, which render it suitable for applications in materials science. In particular, surface functionalized 2D bP and 2D bP heterostructures are promising for electrical, optoelectronic and photocatalytic applications.[1] Herein we report our works on the preparation, characterization and application of 2D bP functionalized with organic molecules or metallic nanoclusters, or modified by an unconventional deposition method in oxidizing conditions, and of the potential applications of such nanostructures.

In a first study,[2] we investigated a non-covalent heterostructure of 2D bP with organo-boron derivatives of a conjugated fluorescent molecule. Experiments and simulations showed an overall increased stability of both moieties in the heterostructure, and functionality as a fluorescent probe for molecular oxygen.

In a second study,[3] we report a study on the epitaxial ordering, kinetics and energetics of a Van der Waals (vdW) epitaxial system of 2D bP and tetracosane (n-alkane with 24 C atoms). Electrostatic force microscopy also proved that the epitaxial nanolayers behave both as a passivating agent and as an electrical insulator (nanodielectric), setting the basis for the possible use of the heterostructure in 2D bP based metal-insulator-semiconductor (MIS) systems.

A third work[4] focuses on the use of electrospray to deposit nano-flakes of bidimensional oxidized bP with a P_2O_5-like crystallographic structure and a large surface area. Piezoresponse Force Microscopy (PFM) demonstrated the electro-mechanical responsivity of the so obtained 2D P_2O_5 nano-flakes, opening towards their possible implementation for energy harvesting/conversion applications.

A final work focuses on 2D bP functionalized through a "stabilizer-free" heterogeneous reaction, leading to an optimal nanostructuring of Au. The soft-pairing/coordination of surface P and Au(I) atoms at the interface was demonstrated. This system holds promise for catalytic applications, such as electro-, photo- or photoelectro-chemical catalysis.

The authors thank the European Research Council (ERC) under the EU H2020 program for funding the project PHOSFUN by an ERC Advanced Grant to Maurizio Peruzzini (GA 670173).

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BODIPY-functionalized Quantum dots platform for high efficiency FRET processes

A. Panniello[a], C. N. Dibenedetto[b, a], M. Trapani[c], M. Cordaro[d], E Fanizza[b, a], C. Ingrosso[a], R. Tommasi[e, a], E. Collini[f], A. Agostiano[b, a], M.L. Curri[b, a], M. Castriciano[c], M. Striccoli[b]*

[a] Istituto per i Processi Chimico Fisici del CNR (IPCF-CNR), c/o Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", Via Orabona, 4 - 70126 Bari (Italy);[b] Dipartimento di Chimica, Università degli studi di Bari ''Aldo Moro'', Via Orabona, 4 - 70125 Bari (Italy);[c] Istituto per lo Studio dei Materiali Nanostrutturati del CNR (ISMN-CNR) c/o Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Viale F. Stagno D'Alcontres31, 98166 Messina (Italy);[d]Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali Università degli Studi di Messina, Viale F. Stagno D'Alcontres31, 98166 Messina (Italy);[e] Dipartimento di Scienze Mediche di Base, Neuroscienze e Organi di Senso, Università degli Studi di Bari "Aldo Moro", Piazza G. Cesare 11-70124 Bari (Italy); Dipartimento Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova (Italy)

Recently, a growing interest has been devoted to the synthesis and organization of nanostructured materials. Intensive research has focused on the fabrication of QDs based organized hybrid structures in solid state, which have shown new properties due to the collective interactions of nanoparticles or at the interface with molecular dyes. In particular, QDs with controlled size and shape coupled and/or functionalized with suitable organic chromophores demonstrated efficient energy transfer (ET) and processes [1]. To promote effective energy transfer in FRET architectures, the distance between the organic fluorophore and the QDs needs to be optimized by a careful system engineering.
The aim of this work is the fabrication of a high FRET efficiency system, both in solution and in solid state, formed by colloidal CdSe QDs and fluorescent BODIPY dyes. In this context, BODIPY dyes bearing amino-terminated functionalities are used in virtue of the high affinity of amine groups in coordinating the QD surface. Monoaminostyryl substituted BODIPY (MASB), with an amino moiety, and diaminostyryl functionalized BODIPY (DASB), a bidentate dye bearing two amino groups, are selected as acceptors in the FRET systems with respect to the donors CdSe QDs. A pre-functionalization procedure of the QDs surface with a short amine ligand demonstrates to favour the interaction with the organic fluorophores in solution. The successful coordination of the MASB to the QD surface, accomplishing a short donor–acceptor distance, provides effective energy transfer already in solution, with efficiency of 76 %. The efficiency further increases in the solid state where the QDs and the dye are deposited as single coordinated units from solution, with a distance between the fluorophores down to 2.2 nm, demonstrating the effectiveness of the coupling strategy. The overall results demonstrate the effectiveness of the tight coupling of the dye at the QD surface in obtaining a FRET architecture with high efficiency both in solution and in solid state, which can be successful employed in sensor devices [2]. In addition, the very short distance between donor and acceptor can promote the investigation of possible coherent effect in the energy transfer process involving the two fluorophores.

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A deep description of the electronic properties of Ti sites in Ziegler-Natta catalysts from advanced spectroscopic methods

A. Piovano,[a,b] M. Signorile,[a] L. Braglia,[c] P. Torelli,[c] A. Martini,[a] T. Wada,[b,d] G. Takasao,[d] T. Taniike,[b,d] E. Groppo[a,b]

[a] Department of Chemistry, INSTM and NIS Centre, University of Torino, Italy; [b] Dutch Polymer Institute, The Netherlands; [c] CNR-IOM, TASC Laboratory, Trieste, Italy; [d] Japan Advanced Institute of Science and Technology, Ishikawa, Japan.

Although Ti-based Ziegler-Natta (ZN) catalysts play a major role in the polyolefins market, a true understanding of their properties at the molecular level is still missing.[1]

In this work, we have coupled diffuse reflectance (DR) UV-Vis and Ti $L_{2,3}$-edge NEXAFS spectroscopies to thoroughly investigate the electronic properties of the Ti sites in two different ZN catalysts, synthetized either by mechanical or chemical protocols (according to the typical industrial practice).[2] The investigation has started from the pre-catalysts (as shown in Fig. 1), where the electron density on the Ti sites correlates with the energy barrier for olefin activation during the polymerization reaction.[3] Our analysis has revealed that in both samples the Ti sites are octahedrally coordinated with six Cl^- ligands all around, but with slight differences in structural parameters and in the effective charge (slightly more positive in the chemically prepared catalyst).

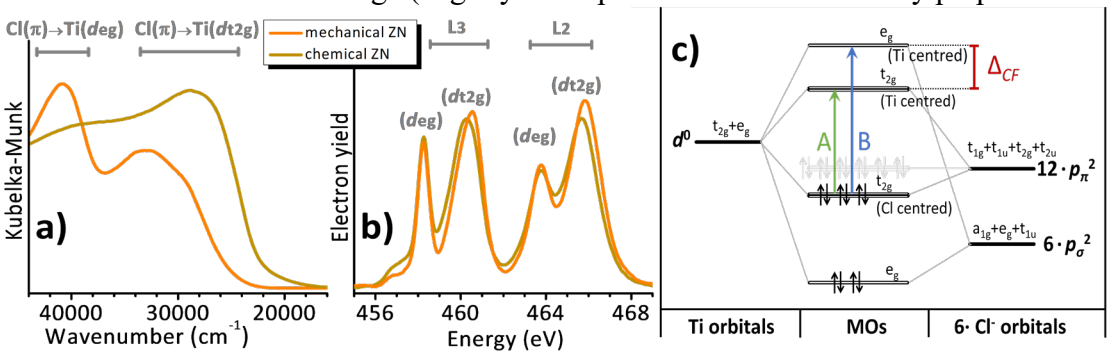

Figure 1. Parts a and b) DR UV-Vis and Ti $L_{2,3}$-edge NEXAFS spectra of the two ZN pre-catalysts. Part c) Simplified molecular orbitals diagram for a Ti^{4+} metal center in an octahedral field with six Cl^- ligands.

Then, thanks to specifically developed experimental setups,[4] for both catalysts we have monitored in situ the activation by AlR_3 (Fig. 2), and the evolution upon ethylene polymerization.

All the experimental results have complemented by theoretical simulations, in order to accurately describe the structure of the Ti active sites.

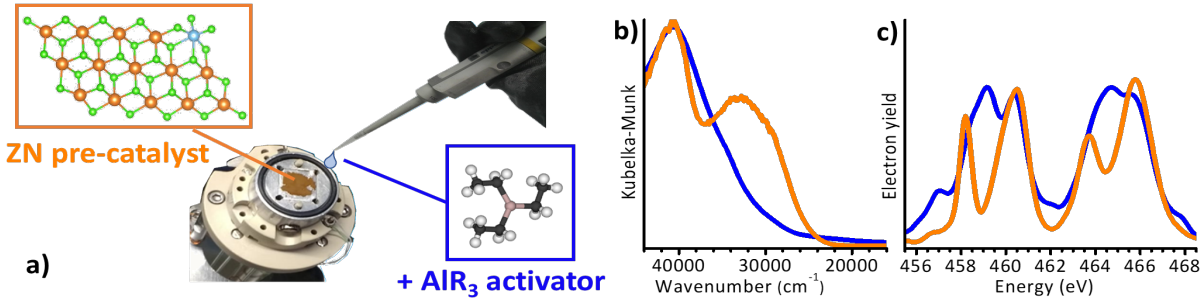

Figure 2. Part a) Activation procedure of ZN pre-catalyst by AlR_3 activator, with theoretical models. Parts b and c) DR UV-Vis and Ti $L_{2,3}$-edge NEXAFS spectra upon reaction of ZN pre-catalyst with AlR_3.

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Insights into biologically-relevant calciprotein particles: effect of stabilizing agents on the formation and crystallization mechanisms

Rita Gelli[a], Valentina Pucci[a], Francesca Ridi[a], Piero Baglioni[a]*

[a] Department of Chemistry "Ugo Schiff" & CSGI, University of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino (Italy)

Despite the concentration of calcium and phosphate ions in human serum is supersaturated with respect to hydroxyapatite, the precipitation of calcium phosphate deposits (CaPs) is typically prevented by the presence of proteins which bind Ca^{2+} and phosphate ions or the nascent CaP clusters and inhibit calcification phenomena that would lead to cardiovascular diseases [1]. Among the macromolecules involved in this process, the glycoprotein Fetuin-A is able to form the so-called calciprotein particles (CPPs) by interacting with CaP amorphous clusters and producing colloidal protein-mineral complexes [2]. In pathological situations, the initially formed harmless amorphous spherical complexes (primary CPPs or CPPI) may mature into crystalline particles (secondary CPPs or CPPII), which eventually lead to ectopic calcifications. Understanding from a physico-chemical perspective the mechanism of ripening of CPPI to CPPII and the factors affecting the process is thus fundamental to prevent the surge of vascular calcifications by developing strategies to delay the crystallization and precipitation of CaP in serum.
In this work we inspect the effect of different ions, *i.e* Mg^{2+}, pyrophosphate and citrate, on the formation and crystallization mechanism of CPPs. Synthetic analogs of serum CPPs were prepared at different concentrations of Fetuin-A and inhibitory ions, and their formation and ripening were followed *in situ* by means of turbidimetry and scattering techniques. The morphology of the obtained nanoparticles at different stages of the process was analyzed by means of electron microscopy whereas FT-IR spectroscopy and X-Rays diffraction allowed for the identification of the formed inorganic phases. This multi-technique approach allowed us to identify the most effective ions in preventing the conversion of amorphous CPPI to crystalline CPPII, suggesting novel strategies to inhibit and treat cardiovascular calcifications.

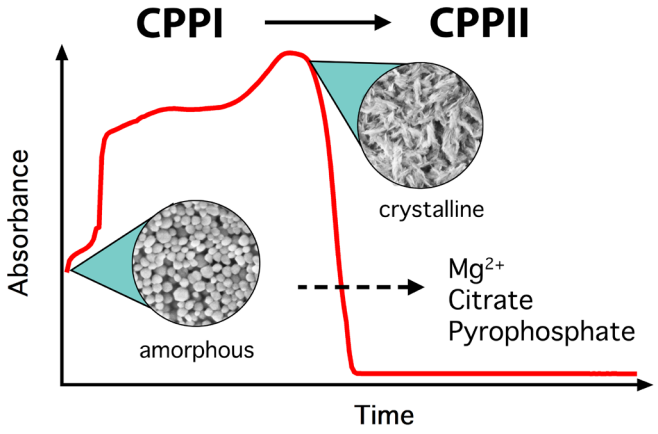

Figure. Schematic representation of the work.

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Regulation of the photosynthetic AB-GAPDH via self-assembly

A. Del Giudice[a], *R. Marotta*[b], *P. Swuec*[c], *L. Galantini*[a], *F. Sparla*[d], *S. Fermani*[e]

[a]*Dipartimento di Chimica, Sapienza Università di Roma, Rome, Italy;* [b]*Istituto Italiano di Tecnologia IIT, Genoa, Italy;* [c]*Cryo-Electron Microscopy Facility, Human Technopole, Milan, Italy;* [d]*Dipartimento di Farmacia e Biotecnologie – FaBiT, University of Bologna, Bologna, Italy;* [e]*Dipartimento di Chimica "G. Ciamician," University of Bologna, Bologna, Italy*

Photosynthetic glyceraldehyde 3-phosphate dehydrogenase (GAPDH) is a key enzyme of the Calvin-Benson cycle, the light-independent part of photosynthesis in which a fixation of atmospheric carbon dioxide into sugars occurs. Through the GAPDH reaction the NADPH produced by the light-dependent electron transport is consumed, leading to the production of the first sugar of the whole photosynthetic process. A tight regulation of GAPDH is therefore necessary to let concurrently proceed the two phases of photosynthesis.

In higher plants two isoforms of GAPDH co-exist in the chloroplast stroma. The homo-isoform, formed exclusively by subunits A (A_4-GAPDH), is inactivated in the dark by the formation of a complex with another enzyme of the Calvin cycle, phosphoribulokinase, mediated by the interaction with the redox-sensitive intrinsically disordered protein CP12 [1-2]. The hetero-isoform, containing A and B subunits, is able to turn off its activity through a self-assembly process that leads to the formation of inactive oligomers, whose stabilization involves the redox-sensitive 30-amino-acid tail called C-terminal extension (CTE) present in the B subunits. Typically, the fully inactive form is considered an hexadecamer A_8B_8, generated by the assembly of four A_2B_2-GAPDH tetramers [3].

With the aim of disclosing the molecular mechanism driving the oligomerization of AB-GAPDH, we performed a structural study of the system in solution by small angle x-ray scattering coupled with size exclusion chromatography (SEC-SAXS) and cryo-electron microscopy (cryo-EM). Both experimental approaches highlighted the coexistence of several $(A_2B_2)_n$ oligomerization states, whose relative proportion depended on the solution conditions (activation/inactivation), showing an unexpected dynamicity (Fig. 1a). The sub-nanometer structure obtained by cryo-EM single particle analysis of the most populated oligomers revealed that pairs of B subunits belonging to adjacent tetramers mutually exchange their CTEs (Fig. 1b), which act as protruding hooks and dock into the active sites of other subunits substantially blocking the access of the substrate.

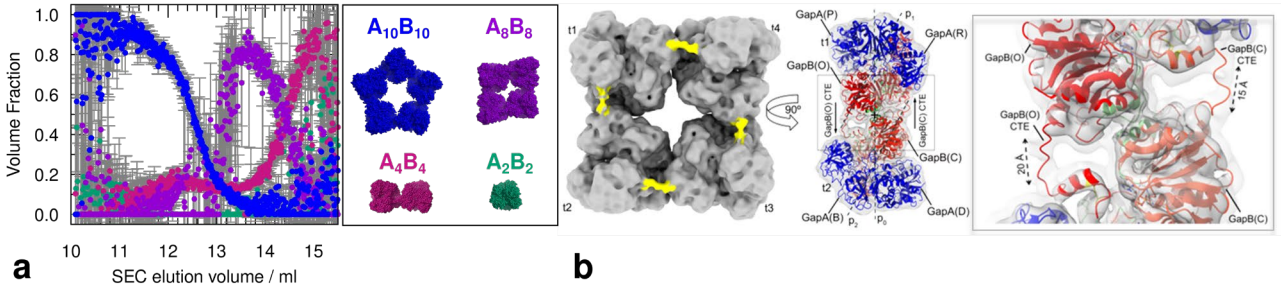

Figure 1. a) Volume fraction of $(A_2B_2)_n$ oligomers in the SEC elution of inactive AB-GAPDH, as obtained by SEC-SAXS data fitting with atomic models. b) Cryo-EM model of A_8B_8 highlighting the CTEs conformation determining enzyme inactivation in the oligomerized state.

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Investigation of Fe-BTC and Z-zni MOFs as carrier for *Aspergillus.sp* Laccase

[a] *Davide Tocco;* [a] *Cristina Carucci;* [b] *Edmond Magner ;* [a] *Andrea Salis*

[a] *Department of Chemical and Geological Sciences-CSGI and CNBS, University of Cagliari, SS 554 bivio Sestu, 09042 Monserrato (CA), Italy.* [b] *Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick, V94 T9PX (Ireland)*

Metal organic frameworks (MOFs) are solid materials which, among several applications, are presently used to host macromolecules, such as enzymes. Among the enzymes involved in industrial processes, due to their low substrate specificity and their high potential for green chemistry applications the interest in use of laccases (LCs, benzenediol: oxygen oxidoreductase, EC 1.10.3.2) is growing steadily. [1] LCs are multi-copper oxidases which oxidize various phenolic compounds by one electron transfer with the concomitant reduction of dioxygen to water. Enzymes immobilization allows to overcome low stability issues associated with free enzymes as well as their reuse or their operation in continuous processes. [2]
Here, two MOFs (ZIF-zni and Fe-BTC MOFs) were used as carriers for the immobilization of the laccase from *Aspergillus sp.* LC immobilization on MOFs occurred *in situ* under mild conditions, e.g. aqueous solution, neutral pH, and at room temperature (Figure 1). The immobilised biocatalysts were characterised through SEM, FTIR, N_2 adsorption/desorption isotherms and TGA. The free LC, LC@Fe-BTC andLC@ZIF-zni biocatalysts were also characterized in terms of specific activity, kinetic parameters (K_M and V_{max}) and (storage and operational) stability.

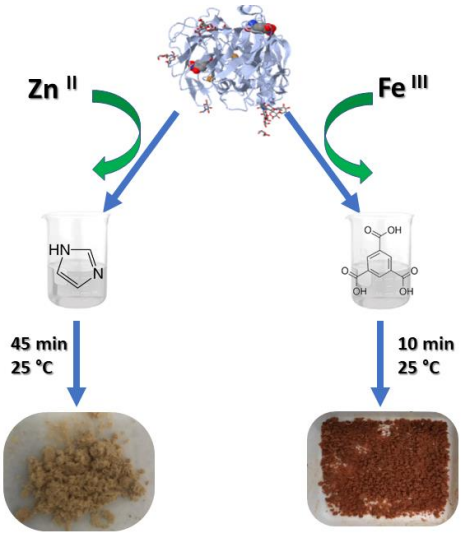

Figure 1: Schematic preparation of the LC@MOF biocatalyst

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Biopolymer-based platforms for cell mechanosensing and regenerative medicine

Pasquale Sacco [1,2], Francesco Lopez [3], Eleonora Marsich [4], Ivan Donati [1]

[1] Department of Life Sciences, University of Trieste, Via L. Giorgieri 5, I-34127 Trieste, Italy[2] AREA Science Park, Trieste, Italy[3] Department of Agricultural, Environmental and Food Sciences (DiAAA) and Center for Colloid and Surface Science (CSGI), University of Molise, Via De Sanctis, I-86100 Campobasso, Italy.[4] Department of Medicine, Surgery and Health Sciences, University of Trieste, Piazza dell'Ospitale 1,I-34129 Trieste, Italy

In this talk I will introduce biopolymer-based networks as platforms for cell mechanosensing and regenerative medicine.
First, chitosan gels will be presented. Chitosan gels are synthetized through a controlled external ionic gelation.[1] Recently it was reported that the physical-chemical properties of chitosan - as well as the molecular weight and the frequency of two building sugars glucosamine (D unit) and *N*-acetyl-glucosamine (A unit) along polymer chain - play a key role for the setting up of cylindrical gels characterized by different mechanical behavior at small/large deformations.[2] The ability of chitosan gels to behave as scaffold for cellular infiltration and ensuing anchoring was recently demonstrated.[3] While keeping constant stress relaxation and systematically decoupling overall stiffness from linear elasticity, we have introduced an energy dissipation term (J/mol), that is the molar energy required to deviate from linear stress-strain regime and enter into plastic region.[4] Strikingly, we have unveiled an inverse relationship between substrate energy dissipation and cell response, with high adhesion/high spreading and low adhesion/no spreading detected for substrates at low and high dissipation energy, respectively. Of note, I will show how combinations of facing 5-consecutive sugars (pentads) composing substrates are essential in damping shear stress, thus behaving as cell traction forces dampers.
Second, chia (Salvia *hispanica)* seed mucilage gels will be presented. Chia seed mucilage represents an emerging biomaterial due to its particular tetrasaccharide (repeating unit) composition. Chia gels have shown very interesting mechanical properties.[5] Alkaline Phosphatase enzyme activity assay and Alizarin red staining demonstrated that chia mucilage did not alter *in vitro* stem cell differentiation. Collectively, this set of experiments revealed an almost inert role associated with chia suspensions, indicating a possible application of chia-based networks as scaffold models to study osteogenesis *in vitro*.[6]

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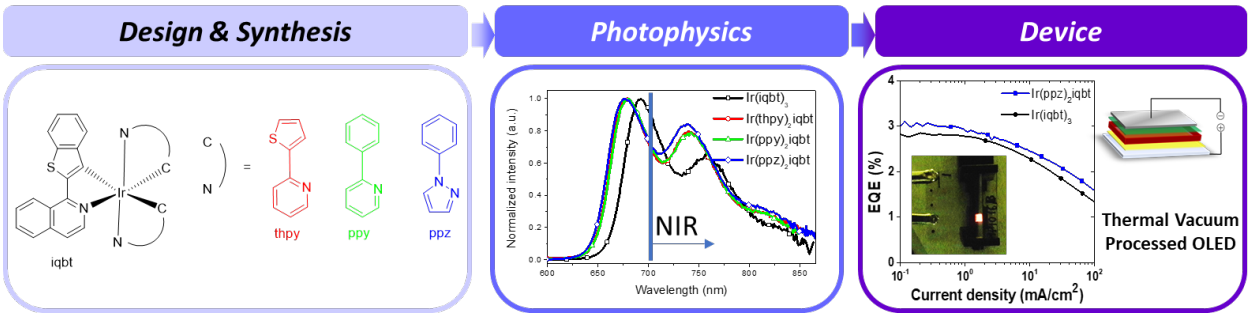
Advancing near-IR phosphorescence with Ir(III) complexes bearing a single emitting ligand: properties and OLED applications

Marta Penconi,[a] *Aravind Babu Kajjam*,[a] *Moon Chul Jung*,[b] *Marco Cazzaniga*,[a] *Clara Baldoli*,[a] *Davide Ceresoli*,[a] *Mark E. Thompson*,[b] *Alberto Bossi*[a]

[a] *Istituto di Scienze e Tecnologie Chimiche "Giulio Natta" (SCITEC - CNR) and SmartMatLab Center, PST via Fantoli 16/15, 20138 Milan and via Golgi 19, 20133 Milano, Italy*[b] *Department of Chemistry, Chemical Engineering and Materials Science, University of Southern California, 3620 McClintock Ave, Los Angeles, CA 90089-1062*

In the recent years, near-infrared (NIR) OLEDs have gained great attention given their potential applications in night-vision-readable displays, sensors, optical communication and medical systems.[1] In this context, octahedral Iridium (III) complexes, the current emitters of choice in commercial OLEDs, are looked as promising candidates. The main strategy to shift towards NIR the emission of a complex is the use of cyclometalated ligands with expanded conjugated pi-system[2] but this approach quickly leads to high-molecular weight derivatives with processing limitation in fully evaporated OLED devices (often more efficient and stable with respect to the solution processed devices). For this reason, heteroleptic complexes, where one of the three cyclometalated ligands is replaced by an ancillary non-chromophoric one, are preferred, resulting in the tune of the electronic energy levels together with a molecular weight reduction.[3]
In this work, we took a step further in the engineering of the Ir(III) complexes by employing only one NIR ligand and two (identical) 'dark' cyclometalated ligands.[4] We have designed an efficient two-step protocol for the preparation of three novel NIR complexes of formula $Ir(C^N)_2(iqbt)$ with a single iqbt (1-(benzo[b]thiophen-2-yl)-isoquinolinate) ligand responsible of the emission in the NIR range. The (C^N) cyclometalated ligands are commercially available and have been rationally selected with higher triplet energy than iqbt. Our approach significantly eases the synthetic effort in terms of purification steps and potential production scale. We demonstrate that the presence of a single iqbt ligand is sufficient to enable efficient NIR phosphorescence with quantum efficiency comparable to that of the homoleptic $Ir(iqbt)_3$. Moreover, the most promising compound has been chosen as dopant to prepare fully-evapored OLEDs which provided efficiencies superior to those of $Ir(iqbt)_3$.



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Divide and Conquer Semiclassical Initial Value Representation: a valuable theoretical tool for vibrational spectroscopy of biological systems

Fabio Gabas[a], *Riccardo Conte*[a] & *Michele Ceotto*[a]

[a]*Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133 Milano, Italy;*

Vibrational spectroscopy represents a very important tool used in several fields to characterize and understand molecular structure and reactivity. Alongside experimental analysis, theoretical predictions have the fundamental role of helping to assign, interpret and understand the energetics and nature of all the vibrational signals in the spectrum. For this reason, a very accurate, reliable and highly predictive theoretical method is strongly desirable.

A very commonly used method, especially when large molecular systems are involved, is represented by the computationally cheap harmonic frequency calculations, often corrected by means of *ad hoc* scaling factors. A viable alternative is represented by the semiclassical initial value representation (SCIVR) approach that exploits the information coming from short molecular dynamics runs to predict vibrational spectra which include not only anharmonicity but also quantum effects. [1-4]

Recently, in our group, we further improved the standard SCIVR method by introducing the Divide-and-Conquer approach (DC SCIVR) which allowed us to study medium and large molecular systems while keeping the capability to catch the full dimensional complex interactions untouched. [5-8]

In this talk I will show vibrational power spectra obtained from the implementation of DC SCIVR with ab-initio molecular dynamics (AIMD). The results I will present involve medium and large size molecular systems of biological interest, including not only isolated small amino acids and nucleobases, but also supramolecular systems and microhydration studies. [7-10] The main goal is to demonstrate that DC SCIVR can represent a solid and valuable theoretical tool for supporting experimental investigations in the field of vibrational spectroscopy.

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First-principles study of Mn and Fe co-doped $BaZrO_3$ as PC-SOFC cathode for the Oxygen Reduction Reaction

Adriana Pecoraro,[a] Mariarosaria Tuccillo,[b] Ana B. Muñoz García,[a] Michele Pavone [c]

[a] Dipartimento di Fisica "Ettore Pancini" Università degli Studi di Napoli Federico II; [b] Dipartimento Ingegneria Chimica Materiali Ambiente Università di Roma la Sapienza; [c] Dipartimento di Scienze Chimiche Università degli Studi di Napoli Federico II

Fuel cells are an efficient way for hydrogen-to-power conversion so representing an appealing green source for energy supply.[1] In this context proton-conducting solid oxide fuel cells (PC-SOFC) have several advantages with respect to their oxygen-ion conducting counterpart, such as lower operational temperatures that prevent thermal expansion and degradation of the constituents, and water formation at the cathode side that avoids fuel dilution.[2] Perovskite oxides, with general formula ABO_3, are typically employed as electrolyte materials thanks to their structure stability and defect tolerance. To date, research has mainly focused on the design of functional materials to be employed as electrolytes. On the other hand, the search for efficient PC electrodes is still underway due to difficulties in finding materials that are mixed proton-electron conductor (MPEC) and – at the same time – efficient catalyst for oxygen reduction (ORR). In this context, in a recent work we investigated Mn and Fe-doped $BaZrO_3$ as potential MPEC electrodes.[3] Both materials showed promising properties with low migration barriers for H^+ transport, but none of the considered dopants alone provided all desired features. Motivated by these results, we explored the synergy of Fe and Mn by considering co-doping of $BaZrO_3$ with both the transition metals. Our results based on state-of-art density functional theory show the ability of such materials to form oxygen vacancies, hydration, and electrical and ORR catalytic properties, all relevant features for its use as PC cathode.

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Energy-Based Molecular Orbital Localization in specific Molecular Regions

Tommaso Giovannini[a], *Henrik Koch*[a]

[a] *Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126, Pisa, Italy*

Localized Molecular Orbitals (LMOs) play an important role in bridging chemical intuition and the molecular wave function, and can also be used to reduce the computational cost of post-Hartree Fock (HF) calculations [1-4]. In particular, for phenomena taking place in a limited spatial location, for instance local electronic excitations, the definition of appropriate LMOs of the specific fragment is crucial to obtain a reliable representation of the property under investigation [5]. In this context, we have recently developed a novel localization procedure able to provide LMOs which span two pre-defined spatial regions of the molecular system [6-7]. Differently from most localization procedures, our developed technique is energy-based, i.e. the LMOs are obtained by minimizing an energy functional, in which the repulsion between two fragments is maximed.
In this contribution, we further extend the localization procedure to the general case of N interacting molecular fragments [8]. By conserving the energy-based feature, we show that the developed algorithm is able to provide Fragment Localized Molecular Orbitals (FLMOs) [8], which can be used to reduce the computational cost of Coupled Cluster approaches when applied to local phenomena.

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TDDFT methods for large systems: new computational schemes and automatic generation of density fitting basis

M. Medves[a], M. Stener[a]

[a]*Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Trieste, Italy*

The *in-silico* design of new nanomaterials with tailored optical properties requires competitive theoretical methods, able to deal with realistic systems. In particular the best compromise between accuracy and computational economy is represented by the Time Dependent Density Functional Theory (TDDFT). The standard resolution of TDDFT equations is obtained through the Casida method, in which energies and intensities of spectral lines are extracted from the Ω matrix, respectively, as eigenvalues and eigenvectors:

$$\Omega F_i = \omega_i^2 F_i$$

For the diagonalization of the Ω matrix the Davidson iterative algorithm is used, which is a very efficient algorithm operating on large Hermitian matrices, but has the limit of extracting a relatively small number of lowest eigenvalues and eigenvectors. An alternative formulation of the TDDFT [1] (named polTDDFT) consists to extract the spectrum as the imaginary part of the polarizability tensor, avoiding Davidson diagonalization:

$$\sigma(\omega) = \frac{4\pi\omega}{c} Im[\alpha(\omega)]$$

PolTDDFT has proven very competitive, allowing calculations on systems consisting of hundreds of metal atoms [2]. The implementation of this method needs the fitting of the induced density, which requires a specific set of auxiliary density fitting functions. Such set consists in a very small number of STO functions, produced by a selection from the near-complete set included in ADF database used to calculate the Coulomb term of the Kohn-Sham Hamiltonian. Such selection is not trivial because in principle all possible combinations should be calculated, then, some approximations have been introduced, as representative sampling, to drastically reduce the combinations to be considered up to a few thousand without losing information. Moreover an appropriate automatic machinery and descriptors are introduced in order to numerically evaluate the accuracy of the produced spectra. Finally, we have considered a very efficient and accurate approximation, named Hybrid Diagonal Approximation (HDA), [3] which allows to employ hybrid functionals and kernels with large saving of computational efforts. For thiolate-protected noble metal clusters it has been shown that hybrid functionals are important to obtain a proper balance between metal and ligand contributions which is a necessary condition to obtain accurate results for optical properties.

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Functionalized Upconversion Nanoparticles for Theranostic

Miletto, I.[a]; Gionco, C.[b]; Paganini, MC.[b]; Giamello, E.[b]; Marchese, L.[a] and Gianotti, E.[a]

[a]Department of Science and Technological Innovation, University of Eastern Piedmont "Amedeo Avogadro", Alessandria, Italy; [b] Department of Chemistry, University of Turin, Torino, Italy

Introduction. Lanthanide-doped upconversion nanoparticles (UCNPs) are nanomaterials capable of converting near-infra-red excitation into visible and ultraviolet emission via a two- or multi-photon mechanism. Studies on UCNPs are attracting increasing interest because of their broad range of applications, spanning from nanomedicine to solar energy harvesting and photovoltaic. To achieve high upconversion efficiency, sensitizer ions must be co-doped with activator ions having closely matched excited states. The most studied sensitizers are Yb^{3+} and Nd^{3+}, which collect and transfer energy to activators, e.g Er^{3+}, Tm^{3+} and Ho^{3+}, which emit green, red and blue light, respectively. Besides the dopants, the correct choice of the host matrix is fundamental as it provides a platform for the energy transfer. In this contribution, preparation and physico-chemical characterization of ZrO_2 and TiO_2 nanoparticles co-doped with Yb^{3+} and Er^{3+} are discussed. UCNPs were functionalized with a silica shell where photosensitizers for photodynamic therapy were anchored, thus creating theranostic nanoparticles that can be triggered by upconversion.

Material and Methods. ZrO_2 UCNPs and TiO2 UCNPs were prepared by hydrothermal process and sol-gel method followed calcination, respectively, where proper amount of dopant ion precursors ($Er(NO_3)_3 \cdot 5H_2O$ and $Yb(NO_3)_3 \cdot 5H_2O$) were reacted with the starting solution of $ZrOCl_2 \cdot 8H_2O$ in water or Titanium isopropoxide in isopropyl alcohol. The concentration of Er^{3+} was kept constant (0.5%-1%) whilst the Yb^{3+} concentration was varied from 1% to 10%.

Results and discussion. Structural and morphological properties were investigated by X-ray powder diffraction, Dynamic Light Scattering and electron microscopies. Absorption and emission UV-Vis-NIR electronic spectroscopies, augmented by upconversion measurements, indicated that the optical features of lanthanide ions were maintained within the host matrices, and that the increase in Yb^{3+} loading leads to a significant increase in Er^{3+} luminescence through upconversion. Successful deposition of silica shell and its functionalization with photosensitizers was assessed by HRTEM and FTIR. Photodynamic activity was assessed by evaluating $^1O_2$ generation efficiency both by direct detection of NIR emission of $^1O_2$ and by an indirect chemical method, evidencing that the photosensitizer maintains its activity upon immobilization on the silica shell. Photosensitizers, whose activity is usually triggered by illumination with visible light, were successfully activated by upconversion.

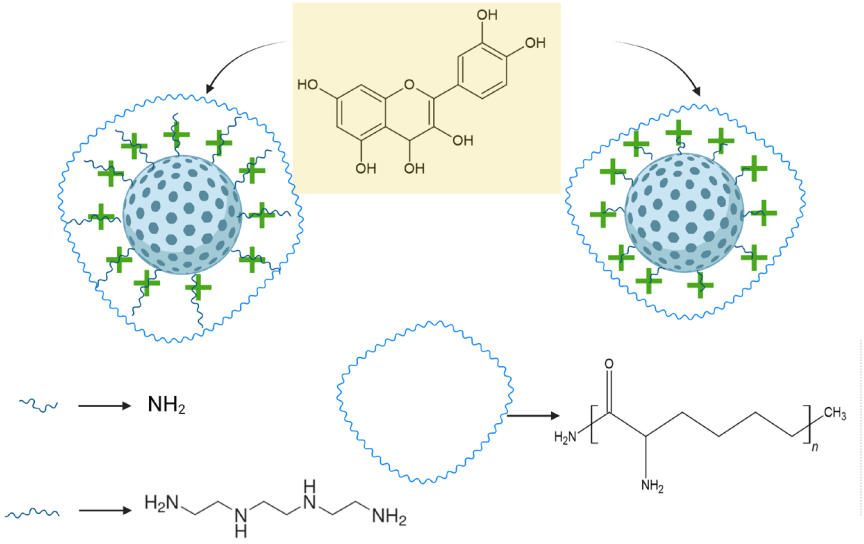
Conclusions. The physico-chemical characterization of Er-Yb co-doped ZrO_2 and TiO_2 UCNPs allowed to disclose structure-properties correlations, in particular with respect to upconversion efficiency of the pristine and functionalized UCNPs and to the disclosure of the possible upconversion mechanisms involved. Photodynamic activity of the functionalized UCNPs was assessed, along with the possibility to trigger it by upconversion.

Drug loaded polymer coated silica nanoparticles as drug delivery route against bacteria

Cristina Carucci[a], Giulia Sechi[a], Marco Piludu[b], Maura Monduzzi[a], Andrea Salis[a]

[a] Department of Chemical and Geological Sciences, University of Cagliari-CSGI and CNBS, Cittadella Universitaria, S.S. 554 bivio Sestu, 09042-Monserrato (CA), Italy[b] Department of Biomedical Sciences, University of Cagliari, Cittadella Universitaria, S.S. 554 bivio Sestu, 09042-Monserrato (CA), Italy

Drug delivery systems (DDS) based on nanoparticles are attracting much attention [1]. Among many fields, in which nanodrug delivery is involved, contrast to resistant and nosocomial bacteria is growing fast [2]. Mesoporous silica nanoparticles (MSNs) can be easily functionalized with chemical groups which allow to enhance, delay, and localize drug release at cell targets [3,4]. Nevertheless, often most common functionalization (i.e. -COOH) still suffer from uncontrollable premature drug release, highlighting the need of stimuli-responsive DDS [5].
Here, MSNs were modified with a pH-responsive cationic polymer poly-L-lysine (PLL) and loaded with quercetin, an antioxidant antimicrobial drug belonging to the class of flavonoids (Scheme 1). The MSNs were initially functionalized with two different amine groups, triethylenetetramine (TETA) and 3-aminopropyltriethoxysilane (APTES) to give MSN-TETA and MSN-NH_2, respectively. The structure and the functionalization of MSN, MSN-NH_2, MSN-TETA. MSN-NH_2-PLL, MSN-TETA-PLL samples were characterized by TEM, SAXS, TGA, FTIR, N_2-adsorption/desorption isotherms, DLS and ELS. Quercetin release kinetics were assayed at different pH. At pH 7.4 release kinetics showed a maximum released concentration of 1.1 μg/mL (MSN-NH_2), 3.0 μg/mL (MSN-NH_2-PLL), 5.0 μg/mL (MSN-TETA) and 4.1 μg/mL (MSN-TETA-PLL). These values are within the range of drug concentration (2-10 μg/mL) in plasma after an oral administration dose of 200-500 mg of quercetin. Finally, the comparison among the UV-Vis spectra of quercetin in PBS and those of the release solutions suggests an improved drug stability upon encapsulation.



Scheme 1. MSN-TETA-PLL and MSN-NH_2-PLL DDS loaded with quercetin

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Engineered Peptides on Gold Nanostructures for Enhanced Targeting Activity in Cancer Diagnosis

F.Biscaglia [a], S. Rajendran,[b] C. Benna,[b] G. Bocchinfuso,[c] P. Conflitti,[c] L. Litti,[a] R. Sommaggio,[b] D. Nitti,[b] A. Rosato,[b] A. Palleschi,[c] S. Mocellin,[b] I.Caligiuri,[d] F.Rizzolio,[d,e] M. Gobbo[a] , M. Meneghetti,[a]

[a] University of Padova, Dept. of Chemical Sciences, Padova, Italy; [b] University of Padova, Dept. of Oncological and Surgical Sciences, Padova, Italy; [c] University of Rome Tor Vergata , Dept. of Chemical Sciences & Technologies, Roma, Italy; [d] Pathology unit, Centro di Riferimento Oncologico di Aviano (CRO) IRCCS, via F. Gallini 2, 33081 Aviano (PN), Italy; [e] Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, via Torino 155, 30172 Venice, Italy.

Due to the optical properties, facile surface chemistry and biocompatibility gold nanoparticles (AuNP) have attracted an increasing interest in cancer nanomedicine for theranostic applications. AuNP can passively target tumours by the EPR effect. However, to fully exploiting their potentiality, they have to be conjugated to active targeting ligands which could improve their pharmacokinetic and pharmacodynamic profiles [1]. Among many targeting ligands, peptides have achieved great success for their low toxicity and immunogenicity as well as for their established synthesis and modification methodologies at reasonable cost [2]. In this context, the aim of the present communication is to show that Gold Nanostructures decorated with peptides properly engineered to optimize the association with the cell receptor can achieve better targeting activity also with respect to nanostructures functionalized with specific antibodies.

Nanostructures were prepared from naked AuNP obtained by Laser Ablation in Solution, encoded with a Raman reporter, to show very intense Surface-Enhanced Raman Resonance Scattering (SERRS) signals [1], and conjugated to engineered peptides [2, 3]. Several peptide analogues were synthesized to investigate the optimal presentation of the targeting peptide on the nanostructures, in terms of the peptide exposure and their orientation to achieve a good association with the receptor. Targeting properties were assessed, by recording the Surface enhanced resonance Raman scattering signals of individual cancer cells, and experimental results were combined to Molecular Dynamic Calculations and spectroscopic analysis. Finally, the stability to proteolysis of the targeting peptides, an important issue for in vivo applications, was evaluated by incubation of the nanostructures with different proteolytic enzymes and human serum, finding that the engineered peptides on the surface of nanoparticles are protected from the enzymatic degradation, and continue to be fully active [4].

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Cubic and lamellar mesophases obtained from algal biomass as drug carriers with high potentiality

I. Clemente,[a,b] C. Bonechi,[a] G. Tamasi,[a] C. Rossi,[a] S. Ristori[b]

[a] Department of Biotechnology, Chemistry and Pharmacology, University of Siena & CSGI, Italy; [b] Department of Chemistry "Ugo Schiff", University of Florence & CSGI, Italy

Lipids are a class of molecules with rich polymorphism that results in a wide range of possible supramolecular aggregates, mainly influenced by the lipid class and packing parameter, which determine the possible values of interfacial curvature and thus the attainable supramolecular symmetries. Such systems can be broadly differentiated in two large categories, lamellar and nonlamellar lipid structures. Lamellar aggregates are characterized by the presence of one or multiple bilayers self-assembling with vesicular morphology. Nonlamellar mesophases are lyotropic liquid crystalline systems which differ from liposomes and other globular aggregates in dilute regimes due to their inner ordering.

It is known that a rich variety of biocompatible nanosystems can be obtained from natural lipids, to be exploited as delivery agents for bioactive compounds with enhanced carrier-target compatibility. Nevertheless, carrying out an in-depth characterization of the structural arrangement in such systems can be rather complex. Due to their packing parameters several classes of lipids found in natural sources can self-assemble into nonlamellar structures, the most abundant being triglycerides, whereas phospholipids tend to form lamellar phases.

Here are presented unconventional nanosystems obtained by lipid extraction from the marine microalga *Nannochloropsis* sp., that can be engineered to preferentially accumulate different lipid classes depending on its growth conditions. In the present case this treatment led to two nanovector series, which were slightly different in chemical composition but distinct in structure, one of them mainly exhibiting complex nonlamellar symmetry, the other a more commonly found lamellar phase [1]. The physico-chemical characterization of these nanostructures was carried out and both series were evaluated as potential carriers for natural lipophilic antioxidants (i.e. curcumin, tocopherol, piperine), whose commercial use is traditionally hindered by their poor water solubility. The overall structural arrangement was studied by combination of Dynamic Light Scattering, Small Angle X-Ray Scattering and Cryogenic Transmission Electron Microscopy. The cargo entrapment, the host-carrier and host-host interactions were investigated by spectroscopic techniques (UV–Vis, Nuclear Magnetic Resonance) [1-2].

The physico-chemical characterization of the mesophases evidenced coexisting multicompartment nanostructures, the most predominant one being of cubic symmetry for nonlamellar nanosystems and globular-shaped for lamellar ones. Investigation of cargo localization showed that not only the lipid class, but the loaded molecules as well played an active role in driving the interactions which characterize the supramolecular structure of the aggregates. Indeed, such compounds can intercalate in lipid bilayers and interact with each other in this environment, generating synergist effects and interesting structure-function properties related to drug delivery with high potentiality.

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Role of the FZD10 delivering exosomes in cellular proliferation of gastrointestinal cancer

Rizzi Federica[a,b], Depalo Nicoletta[b], Fanizza Elisabetta[a,b], Ingrosso Chiara[b], Carrieri Livianna[c], Agostiano Angela[a,b], Curri Maria Lucia[a,b], Giannelli Gianluigi[c,d] and Scavo Maria Principia[c]

[a] Department of Chemistry, University of Bari, Via Orabona 4, 70126 Bari, Italy; [b] Institute for Chemical and Physical Processes (IPCF)-CNR SS Bari, Via Orabona 4, 70126 Bari, Italy; [c] Personalized Medicine Laboratory, National Institute of Gastroenterology "S. De Bellis", Via Turi 21, Castellana Grotte, 70013 Bari, Italy; [d] National Institute of Gastroenterology "S. De Bellis", Scientific Direction, Via Turi 27, Castellana Grotte, 70013 Bari, Italy.

Exosomes are extracellular vesicles (EVs) released by cells and characterized by sizes ranging from 30 to 150 nm; they play a relevant role in mechanisms of cell-cell communication, both in physiological and pathological conditions. Indeed, exosomes act as natural carriers of several bioactive cargoes, such as nucleic acids, lipids, metabolites and proteins[1, 2]. Tumor-derived exosomes containing molecules as non-coding RNA, miRNAs, mRNA and oncoproteins, can transfer their cargo to recipient cells, thus triggering new biological processes, including angiogenesis, therapeutic resistance, formation of metastasis, and increase of proliferation activity[2]. Recently, Frizzled 10 protein (FZD10), one of membrane receptors involved in the Wnt pathway, was proved to be actively involved in carcinogenesis of cancers gastroenteric tract. Indeed, FZD10 was found to be overexpressed not only in colorectal cancer (CRC) tissues, but also in exosomes extracted by serum of CRC and gastric cancer (GC) patients[3].
Here, we demonstrated that both the FZD10 and its messenger RNA (FZD10-mRNA) are delivered by exosomes derived from different gastrointestinal cancer cell lines, namely, metastatic SW-620 colon cancer cells, hepatocellular carcinoma cell line (HLF), gastric carcinoma cells (N-87), human gastric carcinoma cells (HGC-27), and human intrahepatic cholangiocellular carcinoma cells (HUCCT-1). The presence of the FZD10 onto the surface of the tumor-derived exosomes was investigated by using a TEM grid as support for deposition of Au NPs decorated with FZD10 antibody. Furthermore, a substantial decrease in the FZD10 and FZD10-mRNA level was observed in FZD10-mRNA silenced cells and in their corresponding exosomes. Concomitantly, a significant reduction in viability of the silenced cells was achieved. Interestingly, the treatment of silenced cells with the exosomes extracted from culture medium of the same untreated cells induced the restoration of the cell viability and, also, of the FZD10 and FZD10-mRNA level. The overall results suggest that the FZD10 and FZD10-mRNA delivering exosomes may act as messengers of tumor reactivation even in quiescent cells and they may play an active role in long-distance metastatization[4].

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Superfluorinated Exosomes for Sensitive in Vivo Tracking by ^{19}F-MRI

F. Baldelli Bombelli[a], M. Sancho-Albero[b], N. Ayaz[a], V. Sebastián[b], P. Martin-Duque[c], P. Metrangolo[a], J. Santamaría[b]

[a] SupraBioNanoLab-DCMIC "Giulio Natta", Politecnico di Milano, Milan, Italy[b] Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza, Spain [c]Instituto Aragonés de Ciencias de la Salud (IACS) /IIS Aragón, Zaragoza, Spain.
E-mail: francesca.baldelli@polimi.it

This work addresses the current need for novel sensitive, robust, and selective diagnostic tools for non-invasive in vivo imaging, which are able to improve the medical practice through earlier diagnosis of disease, implementation of targeted therapies, and localization of diseased tissues, etc. Our approach is based on the development of new superfluorinated probes enabling ^{19}F-MRI, as a complementary tool, to be coupled with other diagnostic imaging techniques such as ^{1}H-MRI, Raman and fluorescence imaging, in order to overcome their present shortcomings, particularly in terms of sensitivity. ^{19}F-MRI has emerged as one of the most promising diagnostic tools providing hot spot imaging. In this regard, a clear understanding of *in vivo* behavior of extracellular vesicles, which have been intensively explored as potential efficient delivery vectors inspiring novel diagnostic and therapeutic approaches, has not been achieved, yet, partially due to the lack of tools that allow their real-time in vivo imaging. Here we present the first example of superfluorinated bioengineered exosomes, containing PERFECTA (Figure 1)[1,2], a highly symmetric branched molecule with 36 magnetically equivalent ^{19}F atoms. We demonstrate that PERFECTA-Exos maintain physico-chemical features, functionality and biological fingerprint as native exosomes, but exhibit an intense ^{19}F-NMR signal and excellent ^{19}F relaxation times. *In vivo* ^{19}F-MRI tracking and tumor targeting capabilities PERFECTA-Exos (PERFECTA-Exos) are also proved. We propose PERFECTA-Exos as promising bio-hybrids for tracking the biodistribution and delivery of exosomes throughout the body[3].

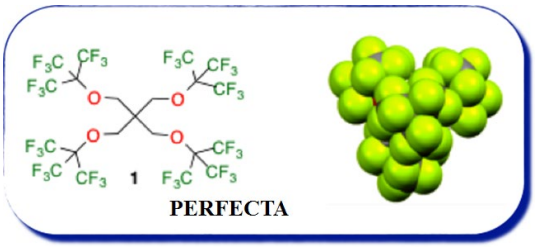

Figure 1: Chemical drawing (left) and single crystal X-ray structure of PERFECTA (right).

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Inkjet Printing Quasi-Miscible Droplets for Pseudo-Planar Organic Heterojunctions

Giuseppe Arrabito,[a] Ana-Gianina Gereanu,[a] Camillo Sartorio,[a] Aurelio Bonasera,[a,b] Giuliana Giuliano,[a] Sebastiano Cataldo,[a] Michelangelo Scopelliti,[a,b] and Bruno Pignataro,[a,b]**

[a]*Department of Physics and Chemistry-Emilio Segrè, University of Palermo, Viale delle Scienze, bdg. 17, 90128 Palermo, Italy;* [b]*INSTM-Palermo Research Unit, Viale delle Scienze, bdg. 17, 90128 Palermo, Italy.*
**emails: giuseppedomenico.arrabito@unipa.it; bruno.pignataro@unipa.it.*

The control of droplet mixing is of great interest for fundamental science (e.g. biomolecular analysis, molecular diffusion, analytes separation) and emerging technologies in lab-on-chip devices (e.g. multiplexed biochips, micro total analysis systems, point-of-care diagnostics) [1]. In this scenario, printing methodologies are a scalable approach for droplets production, resulting in bespoke life-inspired platforms applicable to a vast range of disciplines [2], e.g. materials sciences, sensors, flexible electronics, and biotechnologies. Based on the rapid development of printing techniques for the fabrication of photovoltaic devices [3], this work shows an innovative platform involving inkjet printing to fabricate pseudo-planar heterojunction (PHJ) organic solar cells (OSC) on ITO/PET [4]. The process is based on the sequential deposition of two quasi-miscible inks containing poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl-C_{61}-butyric acid methyl ester (PCBM), the model donor/acceptor couple for OSCs. The optimization of the printing process consists in finding a suitable ink formulation (chlorobenzene based for P3HT and chlorobenzene:dichloromethane in the ratio 1:1 for PCBM), droplet velocity (about 7-8 m/s), droplet spacing (55 μm), ultimately leading to satellites-free spherical picolitre-scale droplets which result in a continuous film on the ITO/PET support. The chemical analysis of the PCBM-on-P3HT printed film is realized by atomic force microscopy, X-ray photoelectron spectroscopy and fluorescence spectroscopy. The morphology is characterized by a continuous and low roughness surface at the center of a printed droplet (average roughness is about 1.3 nm), whereas nanometric aggregates at the droplet border are observed, as a result of Marangoni flows mainly involving PCBM molecules. Such instabilities causing molecular recirculation to the droplet border agree with models developed for bisolvent droplets evaporation [5]. XPS depth profile under mild sputtering conditions (1 kV) permits to analyze the two printed layers, demonstrating the lack of the separation of the P3HT and PCBM layers due the occurrence of complete mixing. The almost complete quenching of the P3HT fluorescence emission band at about 655 nm due to the PCBM layer printed on top of P3HT confirms the effective formation of an interface between the two films. The characterization of the solar cell device allows demonstrating the goodness of the proposed approach, since the extracted parameters are quite similar (in particular the power conversion efficiency) to those realized in a previous reference study where spin coating deposition of the same materials is carried out in a glove box under inert nitrogen atmosphere [6]. In conclusion, this study is a first step towards the analysis of functional interfaces for the realization of a new class of inkjet printed PHJs and, in general, quasi-miscible printed interfaces.

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Cu-functionalized hydroxyapatites: a study of their physico-chemical properties and their potential as electrocatalysts

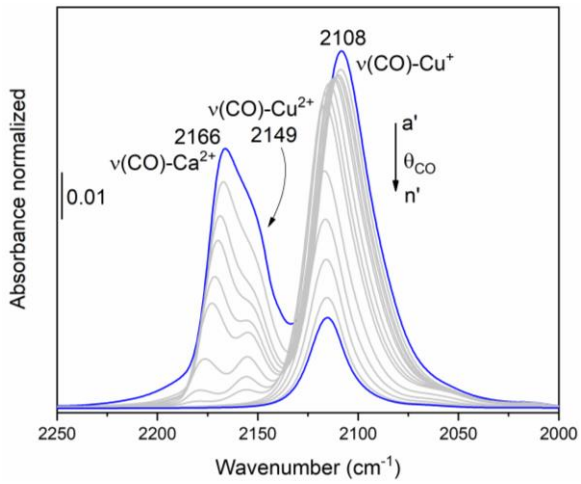
Guillermo Escolano Casado[a], Pavlo Ivanchenko[a], Vedran Milosavljevic[b], Amirmansoor Ashrafi[b], Geo Paul[c], Chiara Bisio[c], Lorenzo Degli Esposti[d], Michele Iafisco[d] and Lorenzo Mino[a]

[a]Department of Chemistry & NIS Centre, Università di Torino, Torino, Italy; [b]Department of Chemistry and Biochemistry, Mendel University, Brno, Czech Republic; [c]Department of Science and Technological Innovation, Università del Piemonte Orientale, Alessandria, Italy; [d]Institute of Science and Technology for Ceramics (ISTEC), National Research Council (CNR), Faenza, Italy.

Nowadays, the search of new families of green- and biocompatible catalysts is a field of great interest and still to exploit. From this point of view, the hydroxyapatites are one of the most interesting materials, due to their inherent biocompatibility, since they constitute the mineralized parts of the human body [1]. Moreover, they have shown applications in the agriculture field and in catalysis, especially when the hydroxyapatites are doped with some metal cations or metal nanoparticles like Cu^{2+} [2, 3].

In this work, hydroxyapatite nanoparticles enriched with Ca^{2+} at the {010} facets (HA_CaRich), were prepared [4] Then, a cationic exchange was performed into the surface of the HA [3], soaking the HA in copper nitrate solutions at different concentrations: 0.01 M (HA_Cu_0.01), 0.05 M (HA_Cu_0.05), and 0.1 M (HA_Cu_0.1).

The total amount of Cu^{2+} in the samples was measured by ICP-OES, elucidating that the maximum surface exchange was reached already in the HA_Cu_0.05 sample with a total Cu content of 7.7 wt%. General structural characteristics were obtained combining X-ray powder diffraction and solid-state nuclear magnetic resonance, confirming that the copper exchange occurred at the surface without altering the bulk structure.



An insight on the surface structure of the different HA was obtained by FT-IR spectroscopy of adsorbed probe molecules. CO was used owing to its capacity to detect both Ca^{2+} and Cu^{2+} cations. The Figure shows the set of spectra collected at different CO coverages for the sample HA_Cu_0.01. Three main bands are present ascribed to the interaction of CO with residual Ca^{2+} surface cations and with two different copper sites (Cu^{2+} and Cu^{+}). For HA_Ca-Rich sample, only the band due to ν(CO)-Ca^{2+} was detected. Conversely, for HA_Cu_0.05 sample only the bands due to Cu carbonyls were present.

Finally, the catalytic activity of the samples was studied by cyclic voltammetry toward the electrochemical reduction of H_2O_2. A gradual increase in the reduction peak of H_2O_2 was observed with increasing Cu contents.

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Laser irradiation of Bio-waste derived carbon as anode for Li-ion batteries

M. Curcio[a,b], A. De Bonis[a,b], S. Brutti[b,c], R. Teghil[a]

[a] Department of Science, University of Basilicata, Viale dell'Ateneo Lucano 10, 85100 Potenza, Italy; [b]GISEL - Centro di Riferimento Nazionale per i Sistemi di Accumulo Elettrochimico di Energia, INSTM via G. Giusti 9, 50121 Firenze; [c]Department of Chemistry, University of Rome ''La Sapienza'', Piazzale Aldo Moro 5, 00185 Rome, Italy

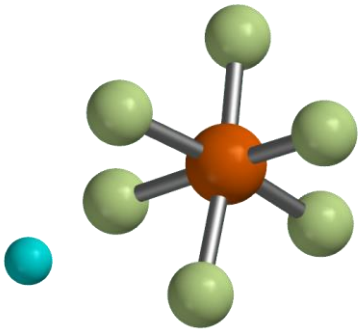
Hydrothermal carbonization (HTC) of biomasses is widely used to obtain hydrochars and can be followed by pyrolisis for producing microporous materials with high carbon content (> 90-95 wt%). The resulting materials can be a valid substitute of graphite in Li-ion batteries (LIB). It is characterized by low crystallinity, high surface area, good cyclability and high lithium intake. Laser irradiation in liquid of these carbonaceous particles can be a useful and simple way to tune morphological and compositional features for improving carbon performances in batteries.
In this work hazelnut shells have been used as starting materials for HTC and the pyrolized matrices. The effect of different thermal treatments on hazelnut shells were investigated in order to obtain a disordered carbon with physic-chemical characteristics suitable for using it as anode material for LIB. Once achieved the best preparation conditions a further modification was made via laser irradiation in acetonitrile by using a frequency doubled Nd:YAG laser with a pulse duration of 10 ns.
Irradiated carbonaceous particles present higher active surface and nitrogen functionalization as a result of the irradiation process. The electrochemical performances of pyrolised carbon before and after laser irradiation were tested by galvanostatic technique, demonstrating the beneficial effect of laser irradiation.

Thermodynamics of the hydrolysis of lithium salts: pathways to the inorganic SEI components

Simone Di Muzio,[a,b],Sergio Brutti[a,c,d], Annalisa Paolone[a]

[a]Istituto dei Sistemi Complessi-CNR Sapienza; [b]Dipartimento di Scienze Fisiche e Chimiche-Università degli Studi dell'Aquila; [c]Dipartimento di Chimica Università di Roma La Sapienza,[d]GISEL-INSTM

In recent years, large efforts have been devoted to the search and improvement of innovative batteries. Lithium-ion types (LiBs) are more expensive than others but their properties, in terms of electrochemical stability, energy densities and number of cycles, are more promising [1].
One of the most common lithium salts used in the electrolytes of this kind of device is Lithium hexafluorophosphate ($LiPF_6$).



This inorganic salt can react with traces of undesired water, giving rise to decomposition by-products, that may precipitate as a part of the solid-electrolyte interphase (SEI), inevitably present in batteries [2]. The hydrolysis of fluorinated salts plays a key role in the formation of the SEI layer: to this end we studied the thermodynamic of this process by computational methods. We proposed a general approach based on thermochemical cycles and *ab initio* thermodynamics calculations to study the reactions in heterogeneous systems. In fact, the precipitation of insoluble phases from the solvent alter remarkably the chemical evolution of the aprotic electrolyte system in solution. Overall, we proposed a mechanism for the hydrolysis of $LiPF_6$ and we plan to extend it to other different kinds of lithium salts.
This Project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 814464.

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Pickering Emulsions Based on Wax and Halloysite Nanotubes for the Treatment of Archeological Woods

Lorenzo Lisuzzo [ab], Theodore Hueckel [a], Giuseppe Cavallaro [b], Stefano Sacanna [a], Giuseppe Lazzara [b], Stefana Milioto [b]*

[a] Molecular Design Institute, Department of Chemistry, New York University, 29 Washington Place, New York, New York 10003, United States[b] Department of Physics and Chemistry "Emilio Segrè", University of Palermo, Viale delle Scienze, pad. 17, Palermo 90128, Italy

In this work we designed a novel green protocol for the treatment and protection of waterlogged archeological woods from ancient shipwrecks. In particular, we developed Halloysite Nanotubes (HNTs) based Pickering emulsions using wax as the inner phase of the oil-in-water droplets and by exploiting paraffin typical thermal properties [1,2]. The physico-chemical characterization of the resulting microparticles was carried out by investigating their morphology through optical microscopy and scanning electron microscopy, which allowed to show the structural features of the prepared hybrid systems and the distribution of the clay at the interface. Micro-differential scanning calorimetry (μ-DSC) was conducted in order to assess whether the thermal properties of the wax are affected after its interaction with the nanoclay. Afterwards, the Pickering emulsions were employed for the treatment of waterlogged wooden structures and they induced a remarkable improvement in terms of stiffness and flexural strength.
It is worth to note that the proposed protocol is eco-friendly and it shows no side effects since water is the only solvent used throughout the entire procedure. Therefore, it represents a promising strategy for the preservation of wooden artworks and it has great possibilities to become exploitable for the treatment of shipwrecks of large size.

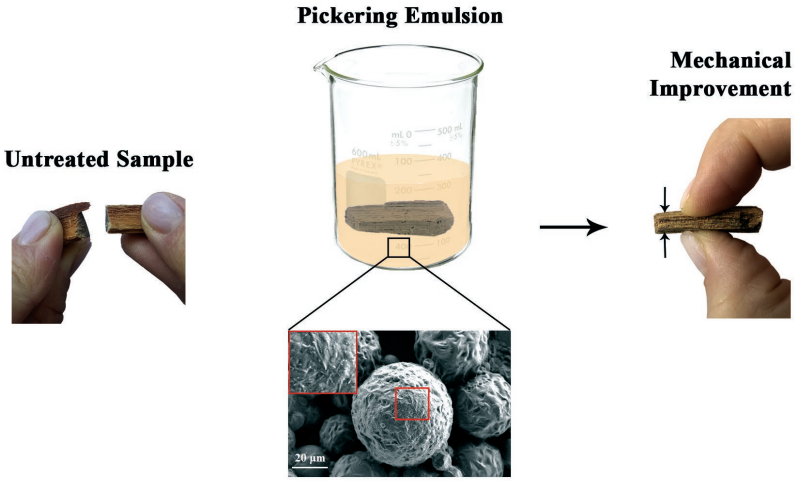

Figure 1. Treatment of archeological woods with Pickering emulsions based on wax and Halloysite Nanotubes.

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Biocomposite Poly(Vinyl Alcohol)/Starch cryogels: green tailorable tools for the cleaning of painted artworks

Vanessa Rosciardi[a,b], David Chelazzi[a,b], Piero Baglioni[a,b]

[a] "Ugo Schiff" Chemistry Department, University of Florence, Italy; [b] CSGI – Center for colloids and surface science, Florence, Italy

Cultural Heritage assets are crucial to mankind, as they are drivers of welfare and economic improvement. If properly preserved, this patrimony can boost job creation, social inclusion and cultural identity. Unfortunately, degradation processes inevitably threaten works of art.

Colloids and material science have been providing effective solutions to preserve works of art in the last decades. In the specific case of cleaning of painted artworks, excellent results have been obtained using highly performing gels based on synthetic polymers[1-2]. However, there is still large room for the formulation of polymer networks that retain optimal cleaning ability but have higher eco-compatibility.

In this perspective, we have developed and studied different biocomposite hydrogels based on poly(vinyl alcohol) (PVA) and rice starch (RS) obtained via freeze-thawing, with water as the only used solvent. The PVA/RS hydrogels have been extensively characterized from a rheological and structural point of view and have been tested as cleaning tools on painted mock-ups with excellent outcomes. To better understand their formation mechanism and the features that derive from it, we then focused on investigating the structural role played by the two polymeric components of starch, i.e. amylose and amylopectin. The hydrogels obtained from different binary (PVA/amylose and PVA/amylopectin) and ternary (PVA/amylose/amylopectin) solutions were subjected to characterization by means of Small Angle X-Ray Scattering (SAXS), Confocal Laser Scanning Microscopy (CLSM), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC) and oscillatory rheometry.

The obtained results have underlined interesting relations between the PVA to biopolymers ratio and the final properties of the hydrogels. We believe that this knowledge could represent a strong base to develop ad hoc materials with tailorable and predictable features, with applications that can go beyond Cultural Heritage preservation.

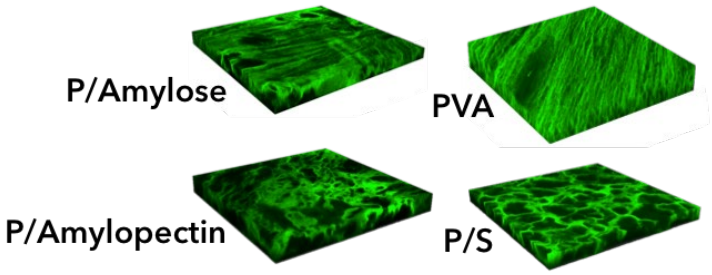

Figure 1 *– Confocal Imaging of cryogels with different compositions (P=PVA, P/S=Biocomposite PVA/Starch gel).*

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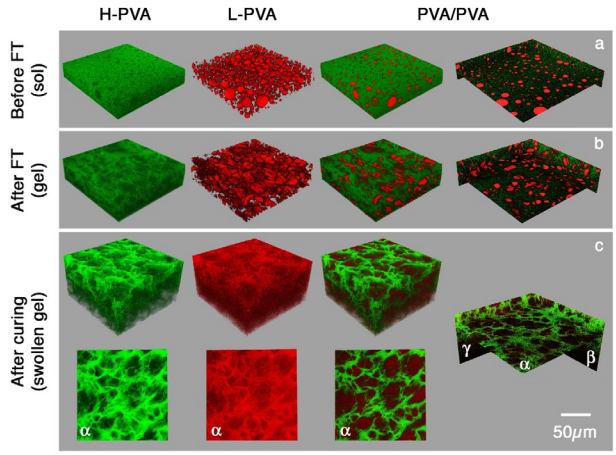
Cleaning Pollock's and Picasso's masterpieces: the physical chemistry behind the scenes

Rosangela Mastrangelo [a,b], David Chelazzi [a,b], Giovanna Poggi [a,b], Emiliano Fratini [a,b], Piero Baglioni [a,b]

[a] *Consorzio per lo Sviluppo dei Sistemi a Grande Interfase, CSGI;* [b] *Università degli Studi di Firenze*

Modern and Contemporary paintings are characterized by rough, clotted and often water-sensitive surfaces. Therefore, the removal of unwanted materials, like grime or aged varnishes, is a very delicate process [1-2]. Our work aims at providing solutions for the effective and selective cleaning of invaluable masterpieces, granting the transmission of our Cultural Heritage to future generations. In this regard, we developed cleaning hydrogels made of polyvinyl alcohol (H-PVA), semi-interpenetrated with a PVA of lower molecular weight (L-PVA) [3]. Gelation was achieved through a freeze-thawing (FT) process. Confocal Microscopy showed that the resulting Twin-Chain Polymer Networks (TC-PNs) have a sponge-like structure and an interconnected porosity, provided by the polymer-polymer phase separation occurred in the pre-gel solution. Small Angle X-ray Scattering (SAXS) and rheology proved that both the presence of L-PVA and the number of FT cycles strongly affect polymer chains conformation and gels' compliance. Fluorescence Correlation Spectroscopy (FCS) gave insights about the polymer dynamics, proving that not only L-PVA behaves as a structural component, but also it can partly diffuse in the gels pores and dangle from the walls, probably enhancing the networks ability to entrap soil. TC-PNs showed high water retentiveness, despite their high equilibrium water content: such gels can be loaded with aqueous solutions or microemulsions, in order to allow the cleaning of different types of grime from water-sensitive substrates. All these features granted unprecedented cleaning performances: hydrophilic grime was successfully removed from the surfaces of "Two" and "Eyes in the Heat" by Jackson Pollock, while aged varnish and wax were easily detached from "The Studio" by Pablo Picasso (Peggy Guggenheim Collection, Venice) [4]. TC-PNs can pave the way to the application of new materials in the restoration practice, proving the effectiveness of a science-driven approach.



Gelation process and morphology of TC-PN, observed through confocal microscopy.

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Adaptive castor-oil based organogels: synthesis, characterization and use for the selective and controlled cleaning of works of art

Giovanna Poggi[a], Harshal Santan[a], Maria Laura Petruzzellis[b], David Chelazzi[a], Emiliano Fratini[a], Giulia Moretti[a], Luciano Pensabene Buemi[b], Piero Baglioni[a]

[a]Department of Chemistry and CSGI, University of Florence, Via della Lastruccia 3 – 50019 Sesto Fiorentino (FI), Italy; [b]Peggy Guggenheim Collection, Dorsoduro 701, 30123 Venice, Italy

The use of organogels represents a valid option for the cleaning of works of art that cannot withstand the application of aqueous systems even when confined in highly retentive carrier, such as hydrogels [1-3].
With the aim of overcoming the limitation of available materials, we have developed a solvent-free and cost-effective synthesis of a new class of gels based on castor oil and isocyanates mixtures [4]. The development of covalent polyurethane bonds during the curing induces significant changes in the viscoelastic properties of the systems which result in strong gels with good mechanical properties.
Changes in reagents' ratio and the use of fillers or other additives allowed us to prepare several formulations whose final properties can be tuned to match those required by specific applications. For applicative purposes, castor oil-based gels can be swollen in organic solvents having a broad range of polarities, such as aliphatic and aromatic hydrocarbons, oxygenated solvents, as well as halogenated solvents. Organogels exhibit different swelling degrees in the selected organic solvents and increase in size upon solvents' uptake, without a significant alteration in their transparency, which is a pivotal feature for conservators as it allows the visual inspection of the artwork's surface during application.
The viscoelastic properties of swollen systems can be finely tuned by varying the composition of the pre-gel mixture and were assessed using rheology. Scattering techniques were used to detail the mesoporosity and the nanoscale structure of the 3D polymeric network before and after solvents' uptake. Overall, these organogels, which adapt to surfaces having different roughness and are easily peeled off from cleaned surfaces without leaving residues on the original artwork, have demonstrated to be an advanced tool for the safe, controlled and efficient removal of unwanted materials from modern and contemporary artworks.

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Nanostructured Fluids For Polymeric Coatings Removal: Surfactants Affect the Polymer Glass Transition Temperature

*Michele Baglioni[a]°, Felipe Hidetomo Sekine[b], Taku Ogura[b,c,d], Sow-Hsin Chen[e], Piero Baglioni[a,e,]°**

[a]Department of Chemistry and CSGI, University of Florence, via della Lastruccia, 3, 50019, Sesto Fiorentino (FI), Italy.[b]NIKKOL GROUP Nikko Chemicals Co., Ltd., 1-4-8, Nihonbashi-Bakurocho, Chuo-ku, 103-0002, Tokyo, Japan[c]NIKKOL GROUP Cosmos Technical Center Co., Ltd., 3-24-3 Hasune, Itabashi-ku, 174-0046, Tokyo, Japan.[d]Research Institute for Science & Technology, Tokyo University of Science, 2641, Yamazaki, Noda-shi, Chiba 278-8510, Japan.[e]Department of Nuclear Science & Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, 24-107, Cambridge, MA 02139, USA.

°No kinship exists among these authors.

Nanostructured fluids (NSFs) are a valid alternative to the use of neat unconfined organic solvents for polymer coatings removal in art conservation. The physico-chemical processes underpinning their cleaning effectiveness in terms of swelling/dewetting of polymer films were identified as key phenomena in this context. The role of organic solvents in polymer swelling and of surfactants in promoting dewetting by lowering interfacial tensions is being clarified [1,3]. However, recent experiments evidenced that surfactants also have an important role in swelling polymer films. To deepen this point, five different amphiphiles were selected, namely: sodium dodecyl sulfate, dimethyl dodecyl amine oxide, hexa(oxyethylene) decyl ether, pentadeca(oxyethylene) dodecyl ether, and methyoxy-pentadeca(oxyethylene) dodecanoate. They were combined with a carefully selected organic solvents' mixture (1-butanol/butanone/dimethyl carbonate) to formulate new NSFs differing for the surfactant only. These NSFs were used to perform cleaning tests on surfaces coated with Paraloid B72® and Primal AC33® and their nanostructure before and after the interaction with polymer films was studied by means of small-angle X-ray scattering. Here, for the first time, polymer swelling induced by surfactants was quantified by means of DSC analyses, which showed that the polymers' Tg was lowered by the migration of surfactants into the polymer films. It was found that nonionics are more efficient than zwitterionic/ionic amphiphiles in polymer swelling, and that, overall, MPD is the most effective among selected surfactants.

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Pd-promoted zeolites for low-temperature NO_x adsorption

S. Morandi[a], L. Castoldi[b], P. Ticali[a], R. Matarrese[b], L. Lietti[b]*

[a]Department of Chemistry, NIS Centre and INSTM, University of Turin, Italy; [b]Department of Energy, Laboratory of Catalysis and Catalytic Processes, Politecnico di Milano, Italy.

The stringent NO_x emission regulations in the automotive sector call for advanced improvements of the NO_x reduction techniques currently adopted in lean-burn engines, i.e. Lean NO_x traps (LNT) and selective catalytic reduction (SCR). However, both techniques are not efficient at low temperatures, as required by recent regulations and by hybrid vehicles where the engine is subject to start and stop cycles. The mitigation of cold-start emissions may be tackled by the use of passive NO_x adsorbers (PNAs), installed in front of the SCR or LNT systems. PNAs store NO_x at low temperature and release the trapped NO_x at higher temperatures, where the downstream NO_x reduction catalysts are able to accomplish the NO_x reduction. In 2016, Johnson Matthey [1] reported efficient formulation for PNA systems based on acidic zeolites doped with Pd.

In this study, commercial zeolites with different framework (Y, ZSM-5, FER and SSZ-13) were doped with Pd (loading 1wt.%) by impregnation in excess of solvent using aqueous $Pd(NO_3)_2$, followed by drying in air at 80 °C and calcination at 750 °C. The samples were characterized by probe molecule adsorption at room temperature followed by FT-IR spectroscopy, micro-reactor gas phase analysis during NO_x storage and subsequent TPD measurements. The aims were to assess the influence of the zeolite frameworks on the Pd phase properties and the relationship between the Pd phase properties and the NO_x adsorption performances. In particular, FT-IR spectroscopy was employed to follow: (i) CO adsorption to characterize the nature and availability of Pd sites; (ii) NO and NO/O_2 adsorption to evidence the species formed during the NO_x storage.

CO adsorption measurements show that the availability of $Pd^{2+/+}$ sites is much higher for Pd/SSZ-13 with respect to the other samples. It is worth of note that the availability of $Pd^{2+/+}$ sites for Pd/Y is almost nil. NO and NO/O_2 adsorption forms mainly nitrosyl and nitrate surface species (Figure 1), whose relative amounts are directly related to the Pd site availability evidenced by CO adsorption. The relative amount of NO_x adsorbed species evidenced by FT-IR spectroscopy follows the order: Pd/SSZ-13 > Pd/FER > Pd/ZSM-5 >> Pd/Y, which is in agreement with the storage capacities evaluated by micro-reactor gas phase analysis and subsequent TPD measurements (Figure 2).

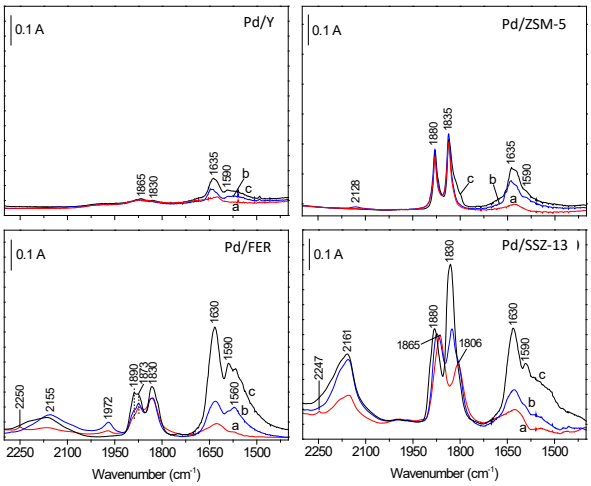

Figure 1. FT-IR spectra of NO (2 mbar, curves a) adsorbed at RT on Pd/Y, Pd/ZSM-5, Pd/FER and Pd/SSZ-13. Curves b and c: NO/O_2 mixture (1:5, p_{NO} = 2 mbar) after 5 and 60 minutes of contact at RT, respectively.

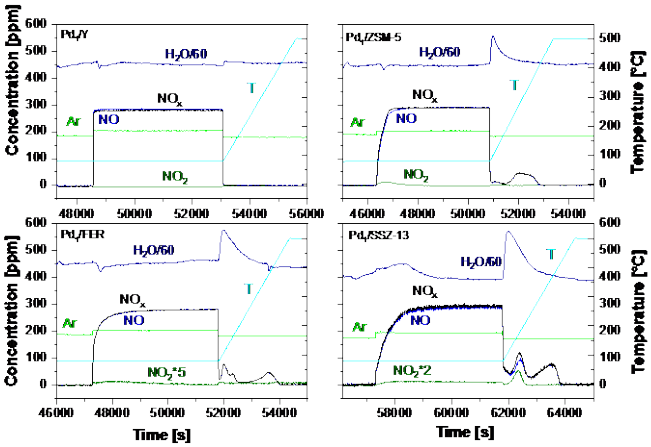

Figure 2. NO/O_2 adsorption at 80 °C and subsequent TPD on Pd/Y, Pd/ZSM-5, Pd/FER and Pd/SSZ-13. Storage phase: NO (300 ppm) + O_2 (3%) + CO_2 (2%) + H_2O (2,5%) in He; TPD in O_2 (3%) + CO_2 (2%) + H_2O (2,5%) in He.

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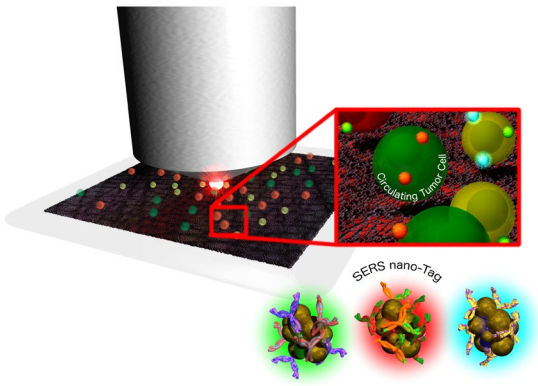
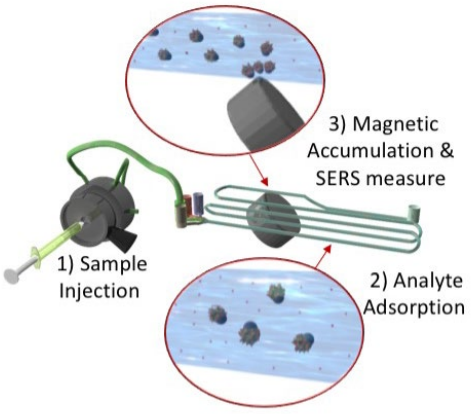
Surface Enhanced Raman Scattering toward applications

Lucio Litti,[a] Moreno Meneghetti[a]

[a] *Department of Chemical Sciences, University of Padova, via Marzolo 1, Padova, Italy*

Surface Enhanced Raman Scattering (SERS) arises from electromagnetic and chemical effects related to excitation of the Surface Plasmons supported on nanostructured, mostly metallic, surfaces. Molecules on such substrates experience orders of magnitude more intense electromagnetic near-fields. This is widely recognized as the main source for the extraordinary intensity gain observed on Raman signals. SERS is nowadays an established ultrasensitive technique, able to reach single-molecule detection. Nanotextured surface composition and morphology, molecule/surface interactions, dielectric environment, are all aspects that strongly influence spectral shapes and intensities of the Raman bands. Understanding all these aspects amplify the potentialities of SERS in real-life applications, which are still largely undeveloped. Through a multidisciplinary approach, the efforts dedicated to implement practical SERS-based sensing techniques will be presented in the fields of biomedical and environmental analysis, toward two peculiar examples. Careful optimization of sample manipulation, data acquisition and processing address the challenge of rare cancer cells detection and counting [1]. Sophisticated magnetic/plasmonic Janus nanoparticles are implemented within a 3D printed microfluidic device for herbicide and anticancer drug quantification in human plasma samples [2]. These two applications can also find a joint development in integrated new devices.





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Organic optoelectronic components in highly integrated systems for plasmonics sensing in food security/quality

Stefano Toffanin[a]

[a] CNR-ISMN (Institute for the Study of Nanostructured Materials, Italian National Research Council), Area Territoriale della Ricerca di Bologna, Via Gobetti 101, 40129 Bologna

The increase of contaminants levels in food has led to negative human health effects from exposure to toxic substances. The interactions between environment and food supply chain that mainly occur at primary production level can cause serious both short- and long-term detrimental effects on human health. Moreover, quality parameters directly affect both the industrial process and the final nutritional and organoleptic properties of the finished products and need to be assessed routinely to increase process monitoring efficiency of the food supply chain and, in turn, competitiveness of the European food processing industry [1].

The smart integration of multiple devices in a single functional unit is boosting the advent of compact optical sensors for cost-effective and on-site analysis. Considering plasmonic sensors, the strict constraints on the detection scheme are hampering the deployment of this extremely powerful sensing technology [2].

The MOLOKO project aims at the manufacturing and implementation of miniaturized organic photonic sensor for plasmonics-based screening of safety and quality parameters for sustainable milk and dairy industry. In particular, the multiplexed and (semi)quantitative detection is expected to be of up to 10 analytes among which food safety parameters e.g. antibiotics (i.e. penicillin, cephalosporin) and toxins (i.e. enterotoxins) and food quality parameters e.g. lactoferrin and caseins.

The rapid and reusable final prototypal sensor is based on an opto-microfluidic detection scheme and designed according to milk production and distribution end-users. These challenging objectives are achieved by the unprecedented integration within the same device platform of multiple key-enabling technologies as organic photonics, nanoplasmonics, immunoassay diagnostics and microfluidic system.

In this contribution, we report on the latest results obtained in the project with particular attention to (i) the scheme of monolithic integration of the different nanostructured device-components resulting in a sensor size as low as 0.1 cm^3, (ii) the proof of concept of the innovative detection scheme in lab environment reporting dose-response curves for analytes of interest and (iii) two specific application scenarios for screening milk at the different levels of the value chain (i.e. cow, farm and plant levels).

This work has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 780839.

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SERS-SPR COUPLING FOR ULTRASENSITIVE DETECTION OF DOPAMINE IN ARTIFICIAL CEREBROSPINAL FLUID.

S. Bettini,[1] R. Pagano,[1] Z. Syrgiannis,[2] C. Ingrosso,[3] G. Giancane,[4] L. Valli[1]

[1] Department of Biological and Environmental Sciences and Technologies, DISTEBA, University of Salento, Via per Arnesano, 73100 Lecce, Italy [2] Simpson Querrey Institute, Northwestern University, Chicago, IL, United States[3] CNR-IPCF Istituto per i Processi Chimico-Fisici, Sez. Bari, c/o Dip. Chimica Via Orabona 4, Bari, 70126, Italy[4]Department of Cultural Heritage, University of Salento, Via D. Birago, 73100, Lecce, Italy

Dopamine (DA) is one of the most important catecholamines largely diffuse in human brain and biological fluids (saliva, urine, blood, serum). DA is a fundamental neurotransmitter governing neural, vascular and hormone communication and functions. DA levels monitoring in biological complex fluids, especially cerebrospinal fluid (CSF), is an intriguing challenge in the frame of early diagnosis of several neural diseases and disturbs (as Parkinson's, Schizophrenia, epilepsy, Huntington's) as well as for therapeutic treatment monitoring and specific drug design. [1] In particular, it is reported that Parkinson's patients CSF is characterized by an important decrease of DA concentration, below 100 pM, whilst the physiological range is known to be 0.5-25 nM. Several approaches have been investigated for ultrasensitive DA detection, both electrochemical and spectroscopic, with limitations regarding the selectivity in one case and the sensitivity in the other [2]. In this contribution, a perylene bisimide derivative (PBI^+, Figure 1A) was selected as active layer due to the well-known affinity towards aromatic amines [3] for the development of a hybrid Layer by Layer (LbL) film based on PBI^+ moieties and citric acid capped Au nanostructures (AuNS, Figure 1B).

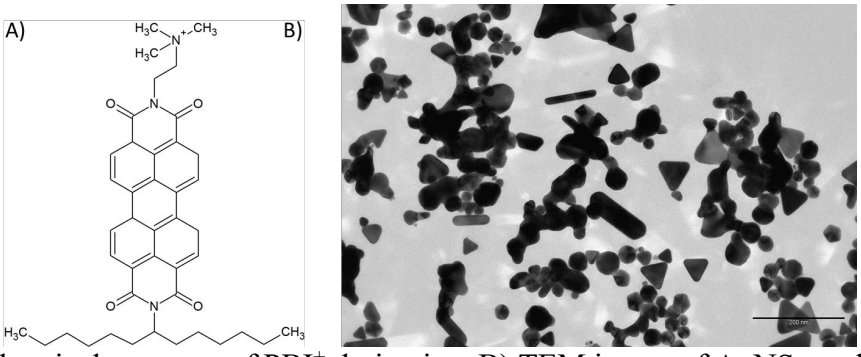

Figure 1: A) Chemical structure of PBI^+ derivative; B) TEM image of AuNS synthetized in this contribution.

The PBI^+-AuNS dyad films are characterized by a clear-cut SERS effect upon 532 nm illumination allowing a strong enhancement of perylene Raman signals. This effect was exploited for the design of a SPR sensing system allowing an important enhancement of SPR sensitivity towards DA down to 1 pM in MilliQ grade water and to about 10 pM in artificial CSF.

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A bimodal imaging probe for combined Raman microscopy and ^{19}F-MRI

Cristina Chirizzi [a], Carlo Morasso [b], Alessandro Caldarone [b], Matteo Tommasini [c], Fabio Corsi [b,d], Linda Chaabane [e], Renzo Vanna [f], Francesca Baldelli Bombelli [a] and Pierangelo Metrangolo [a]

[a] Laboratory of Supramolecular and Bio-Nanomaterials (SupraBioNanoLab), Department of Chemistry, Materials, and Chemical Engineering "Giulio Natta", Politecnico di Milano, Milan, Italy; [b] Istituti Clinici Scientifici Maugeri IRCCS, Pavia, Italy; [c] Department of Chemistry, Materials, and Chemical Engineering "Giulio Natta", Politecnico di Milano, Milan, Italy; [d] Department of Biomedical and Clinical Sciences "Luigi Sacco", Università di Milano, Milan, Italy; [e] Experimental Neurology (INSPE) and Experimental Imaging Center (CIS), Neuroscience Division, IRCCS Ospedale San Raffaele, Milan, Italy; [f] CNR-Institute for Photonics and Nanotechnologies (IFN-CNR), Department of Physics, Politecnico di Milano, Milan, Italy

The development of sensitive multimodal probes is highly required to give information at different levels improving early diagnosis and supporting personalized medicine [1]. Here, we report the ability of a superfluorinated molecule, PERFECTA, to work as bimodal probe for both whole body macroscopic *in vivo* ^{19}F-MRI and microscopic Raman imaging at sub-cellular resolution. This is possible thanks to the unique chemical features of PERFECTA. Indeed, regarding its ^{19}F-NMR characteristics, PERFECTA is characterized by a single and intense peak related to 36 equivalent ^{19}F-atoms (**Fig. 1a-b**) with optimal relaxometric parameters for ^{19}F-MRI. Interestingly, PERFECTA also shows exceptional Raman features, i.e. stretching and bending vibrations (**Fig 1c**), thanks to its high molecular symmetry. This strong and distinctive Raman fingerprint falls in the almost cell-silent 500 – 800 cm^{-1} region allowing its detection without the need of additional staining. *In vitro* studies on microglial cells demonstrated how ^{19}F-labelled cells could be clearly detected by ^{19}F-MRI and Raman imaging, which clearly showed the presence of PERFECTA in the cytoplasm (**Fig. 1d**). Considering the high performance of PERFECTA in both modalities, it was explored *in vivo* in a model of multiple sclerosis. By *in vivo* ^{19}F-MRI, PERFECTA was detected along the spinal cord of EAE mice, where a high infiltration of immune cells was also found, and importantly, the presence of the ^{19}F-probe was also observed by *ex-vivo* Raman imaging in the white matter in correlation with loss of myelin [2]. Of note, beside the direct observation of PERFECTA, the biomolecular composition of the tissue was assessed by RAMAN in label-free mode. The use of PERFECTA as bimodal-probe avoids unpleasant misinterpretations which can greatly help for translation into clinics. Furthermore, intrinsic chemical versatility of this fluorinated tracer may allow further chemical functionalization and future targeting.

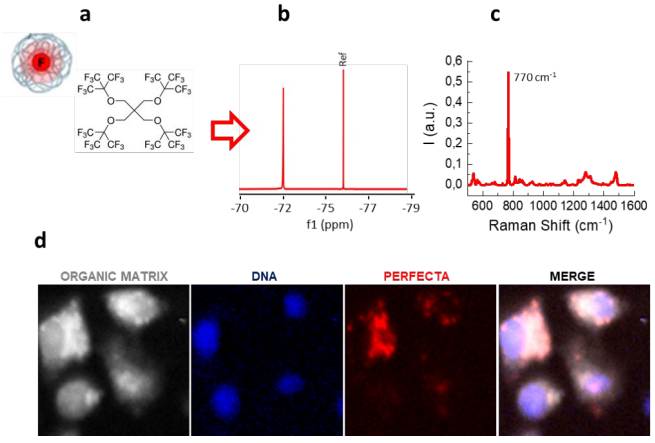

Figure 1. a. PERFECTA was nanoformulated as emulsion of a non-ionic surfactant to obtain ^{19}F-loaded NPs. **b.** Typical ^{19}F-NMR spectrum of PERFECTA together with a reference for quantification. **c.** The Raman spectrum of ^{19}F-nanoformulation shows the characteristic PERFECTA peak at 770 cm^{-1}. **d.** Raman Imaging acquired on ^{19}F-labelled cells after selecting Raman bands of PERFECTA, DNA (787 cm^{-1}) and organic matrix (1450 cm^{-1}).

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Novel pressure sensors based on elastomeric PDLC films

De Filpo Giovanni[a], Baratta Mariafrancesca[a], Tursi Antonio[a], Mashin Aleksander I.[b], Nicoletta Fiore P.[c]

[a] Department of Chemistry and Chemical Technologies, University of Calabria, 87036 Rende (CS), Italy; [b] Applied Physics & Microelectronics, Lobachevsky State University of Nizhni Novgorod, 603950 Nizhni Novgorod, Russian; [c] Department of Pharmacy, Health and Nutritional Sciences, University of Calabria, 87036 Rende (CS), Italy.

New pressure sensitive PDLCs based on a silicone elastomer have been developed. Morphology analysis revealed that liquid crystal droplets inside the film are elliptical in shape with the long axis perpendicular to the surface of the glass supports. Elliptical droplets were obtained by applying an AC (1000 Hz) electrical field during polymerization process (PIPS) of the polymer matrix of PDLCs. Films were characterized by Scanning Electron Microscopy and Polarized Light Microscopy in order to investigate the effect of LC concentration and electrical field strength on the shape, size and LC configuration of droplets. In order to evaluate the PDLC pressure sensitivity, the change of film resistance was investigated as a function of the applied external pressure. Measurements showed a good electrical resistance response, which was proportional to the applied pressure.

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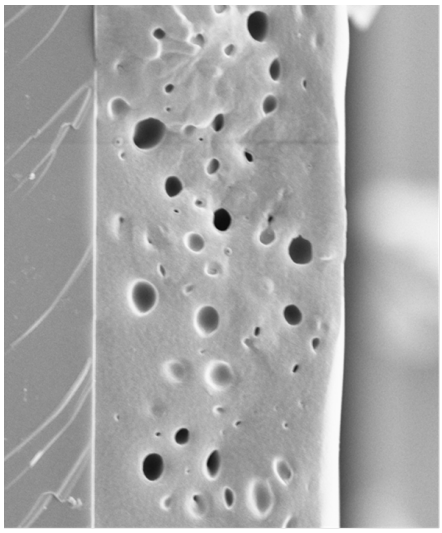
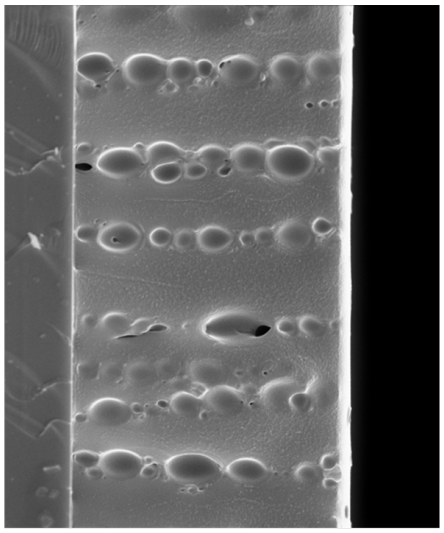
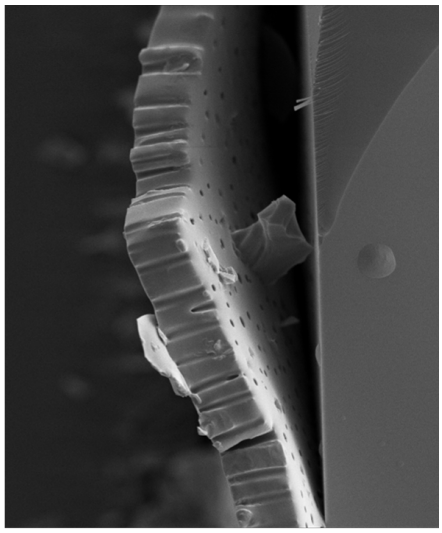


E = 0 V/μm



E = 4.5 V/μm



E = 10 V/μm

Investigating the interfacial solvation properties of the Mg^{2+} ion by operando soft X-ray absorption spectroscopy at ambient pressure and simulations

Francesco Tavani[a], Matteo Busato[a], Luca Braglia[b], Silvia Mauri[b], Piero Torelli[b], Paola D'Angelo[a]

[a] Dipartimento di Chimica, Università di Roma "La Sapienza", P.le A. Moro 5, 00185 Rome, Italy; [b] Istituto Officina dei Materiali (IOM)-CNR, Laboratorio TASC, Area Science Park, S.S. 14 km 163.5, Trieste I-34149, Italy.

Reaching a quantitative knowledge of the structural and dynamic properties of the Mg^{2+} ion would constitute an essential step forward towards the mechanistic comprehension of relevant biological and technological processes. Mg^{2+} is in fact involved in important cellular pathways that belong to all forms of life, many of which have not yet been fully understood, activating enzymes and nucleic acids, promoting their conformational transitions and behaving as a Lewis acid in ATP hydrolysis and RNA folding [1,2]. Further, rechargeable Mg-ion batteries, where common electrolytes such as acetonitrile are employed, are gaining considerable interest as promising candidates for future energy storage systems [3]. However, to date, a complete characterization of the structural properties of the Mg^{2+} ion even in the simplest aqueous and non-aqueous solutions has not yet been obtained. Such difficulties may also be ascribed to the severe experimental difficulties encountered in the use of X-ray based spectroscopic techniques to investigated a low-Z number species such as the Mg^{2+} ion. In fact, although, for instance, X-ray Absorption Spectroscopy (XAS) allows, in principle, one to gain unique structural and electronic information of a given photoabsorbing element in solution, its use to probe the properties of the Mg^{2+} ion in aqueous and non-aqueous solutions has been severely hampered by the requirement of soft X-rays, that need tailored beamline experimental set-ups (such as vacuum conditions and windowless beamlines) and special systems of detection [4].
In this presentation, our group's recent efforts to address the need of new methods that may uncover the solvation properties of the Mg^{2+} ion will be summarized. Specifically, by combining *operando* soft near edge X-ray absorption fine structure at ambient pressure with multivariate curve resolution [5-8], density functional theory and molecular dynamics analyses, we present an innovative method to monitor in real time the chemical changes that take place at the surface of a Mg-containing solid system upon exposure to a series of solvating media, such as water, methanol and acetonitrile.
Within the employed work-flow, quantitative structural and electronic information is retrieved for the reversibly dissolved Mg^{2+} ions in each of the investigated solvents.
Our results pave the way for the application of operando soft XAS to access the often elusive properties of low-Z number metal ions involved in processes of chemical and biological interest.

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Organic light-emitting transistors: advanced materials and innovative architectures towards a real-setting application

Mario Prosa,[a] Salvatore Moschetto,[a] Emilia Benvenuti,[a] Manuela Melucci,[b] Michele Muccini,[a] Stefano Toffanin[a]

[a] Istituto per lo Studio dei Materiali Nanostrutturati (ISMN) – Consiglio Nazionale delle Ricerche (CNR), via P. Gobetti 101, 40129 Bologna; [b] Istituto per la Sintesi Organica e la Fotoreattività (ISOF), Consiglio Nazionale delle Ricerche (CNR), via P. Gobetti 101, 40129 Bologna.

The fascinating combination of light-emitting characteristics and electrical amplification identifies organic light-emitting transistors (OLETs) as key-enabling devices for a wide variety of applications, ranging from displays to sensors. Having dual optical and electrical functionality is the major strength and the major challenge of the OLET technology. Indeed, drastic limitations arise from the poor availability of organic semiconductors (OSCs) that form the active layer, since they are required of high ambipolar charge carrier mobility and high luminescence quantum yields.

In this talk, thienoimide (TI)-ended oligothiophenes are presented as a new class of versatile compounds with suitable characteristics for OLET applications.[1] The outstanding self-assembly capability and their inherent polymorphism allowed an unprecedented control on the processes of thin-film formation. Specifically, the use of NT4N as a quarterthiophene derivative with two TI groups, resulted in OLETs with an electron-to-hole mobility ratio of 78.57, and an optical power of emission as high as 180 nW. The combination of high emission intensity with a pronounced electrical ambipolarity enabled to unravel the full potential of OLETs, as planar devices in which the spatial location of the emission zone can be moved by playing on the operational parameters. Accordingly, the emission stripe of NT4N-based OLETs was demonstrated to be laterally shifted of tens of micrometers from the initial position.

In the search for alternative strategies to circumvent the need for a single ambipolar OSC, one of the most promising approaches arose from the trilayer structure, in which an emissive layer is stacked between two OSC layers having opposite charge-carrier characteristics to provide the ambipolar electrical characteristics to the entire OLET. The properties required for a single OSC were indeed distributed into three different layers.

Despite record efficiencies have been obtained,[2] breaking advances in the OLET technology have been missing for some time due to *i*) the lack of high n-type mobility OSCs, *ii*) the issue that the morphology and the optoelectronic characteristics of the top layer of the stack are influenced by the underlying layers, and *iii*) the complexity to induce the vertical injection of laterally flowing charges into the emissive layer.

In a scenario where the device operation is still poorly understood, an unprecedented comparative analysis was performed on devices based on three different n-type compounds on top of the stack, which allowed us to clarify the complex operation mechanisms occurring in such a complex device

The rational introduction of a vertical-injecting layer ended up in the obtainment of OLETs with advanced characteristics towards the real-setting application of organic photonics and optoelectronics.

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Mixing liquid amphiphiles to prepare organic fluids fully responsive to a magnetic field

Pietro Calandra [a]
[a] *CNR-ISMN, Via Salaria km 29.300, 00015, Monterotondo Stazione (RM), Italy;*

Binary mixtures of liquid surfactants, owing to the amphiphilic nature of the molecules involved, can exhibit nano-segregation and peculiar transport properties: enhanced proton conductivity [1], anomalous 1D diffusion [2], exotic solubilizing properties towards inorganic salts [3] anti-Arrhenian behavior of proton conductivity [4]. Both theoretical (ab-initio) calculations and experiments conducted with various techniques, highlighted that a proton transfer from alkyl phosphates to alkylamines takes place when mixed together, due to the acidic and basic nature of the two molecules involved. This triggers the formation of charged species in liquid phase and an intermolecular association typical of ionic liquid systems. The formation of an inherently anisotropic ion pairs constituting the building block of highly structured ionic liquid nanodomains makes the fluid able to become birefringent when a magnetic field is applied [5]. It is worth of note that the organic-based fluid can react to a magnetic field even if it does not contain any magnetic atom, a fact opening the door to a new field in the physics of fluids.

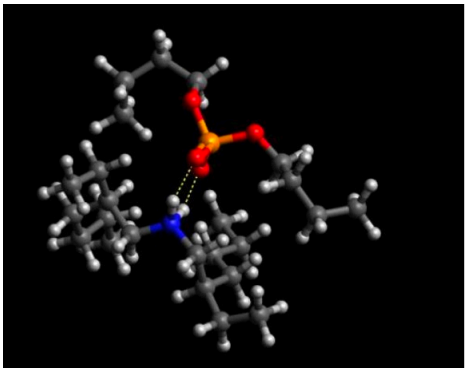

Figure 1: geometry of dibutyl phospfate – bis(2-Etylhexyl) amine optimized by *ab-initio* DFT-b3lyp calculation.

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A Hyphenated Approach Combining Pressure-Decay and In Situ FT-NIR Spectroscopy to Monitor Penetrant Sorption and Concurrent Swelling in Polymers

Valerio Loianno[a], *Antonio Baldanza*[a], *Giuseppe Scherillo*[a], *Rezvan Jamaledin*[b], *Pellegrino Musto*[c], *Giuseppe Mensitieri*[a]

[a] *Dept. of Chemical, Materials and Production Engineering, University of Naples Federico II, Piazzale Tecchio 80, Naples 80125, Italy*[b] *CABHC@CRIB, Istituto Italiano di Tecnologia, Via Largo Barsanti e Matteucci 53, Naples 80125, Ital*[c] *Institute for Polymers, Composites and Biomaterials, National Research Council of Italy, Viale Campi Flegrei 34, Pozzuoli (Na) 80078, Italy*

Polymeric membranes are an attractive solution in the Oil&Gas and petrochemical industries to separate mixtures of chemicals in the gas or liquid state [1]. Compared to thermal-based separation processes, membrane modules require much less energy, they are cheaper and more sustainable. However, structural modification of the matrix induced by the absorbed chemicals generally deplete the separation performances. Sorption induced swelling, glassy-rubbery phase transitions or degradation of the polymeric material are phenomena usually encountered during operation.

In this contribution, a new analytical technique coupling barometry and FT-NIR Spectroscopy in transmission mode is presented to study simultaneously the sorption thermodynamics and kinetics of gases in polymer films and the induced swelling of the matrix [2]. To validate the technique, sorption of CO_2 in a polydimethylsiloxane film 1.5 mm thick is investigated up to 9 bar at 35°C and the results are compared with literature data. Barometry allows the evaluation of the penetrant concentration in the polymer phase as well as the sorption kinetics. FT-NIR Spectroscopy returns the spectrum of the polymer – penetrant mixture from which analytical peaks of the polymeric material and of the low MW compound are retrieved. The former allows the evaluation of the membrane dilation: swelling is found to depend linearly on the absorbance ratio of the investigated dry polymer signal over the same signal after reaching thermodynamic equilibrium with the penetrant gas phase. Moreover, the intensity of the absorbed gas signal at equilibrium is correlated with the concentration values from the barometric analysis and the absorptivity of the penetrant IR signal is calculated. This signal is also used to evaluate the sorption kinetics which is compared with the barometric results.

The new hyphenated technique gives a complete thermodynamic picture of the sorption process of gases in polymer films. The sample is not constrained and its thickness may vary from a few μm to a few mm [3]. FT-NIR spectroscopy also provides valuable information about the molecular environment surrounding the probe: the method is able to describe the problem both macroscopically and microscopically.

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Design and development of multifunctional hybrid surface coatings for advanced and smart applications on textiles

M. R. Plutino

[a] *Institute for the Study of Nanostructured Materials, ISMN – CNR, Palermo, c/o Dep. ChiBioFarAm, Univ. Messina, Viale F. Stagno d'Alcontres 31, Vill. S. Agata, 98166 Messina, Italy.*

Nowadays the versatility of nanotechnological processes in the design of functional hybrid coatings for textiles is of great importance to ensure their efficient and stable deposition onto fabrics with different natures. In this regards, an important contribution to the advancement in textiles coatings was provided by an innovative way to consider the textile polymers besides their conventional use, towards the development of the so-call "technical" or "smart textiles".
In particular, the sol-gel technique is widely investigated thanks to its low-environmental impact together with fascinating properties of the derived thin films, among which high chemical stability, optical transparency, flexibility, improved mechanical, physical, and chemical properties, together with the maintenance of textiles unique properties (i.e. flexibility, breathability, mechanical strength, simple processing, biocompatibility, and washability). The inclusion of specific functional nanofillers in polymeric matrices and/or in combination with appropriate dopants, to be used as functional and eco-sustainable coatings, is a powerful approach towards the development of textiles featuring stringent high-performance and smart requirements specific to a particular use and applications, dealing with hydrorepellent, halochromic, antimicrobial, drug-release, sensing, and flame-retardant activities [1-7]. The characteristic proprieties of sol–gel polymeric materials and their possible employment in the development of widely employed 3D-matrices could be addressed to the synthesis of useful coatings for protection, as well as smart, fire-resistant, and antifouling silica-based coatings. Actually, the inclusion of sensing functions into fabric textiles is a powerful approach towards the development of "smart textiles", allowing the development of wearable sensors, i.e. new systems able to react and adapt to specific external environment stimuli from their surroundings. The use of polymers combined with anti-oxidant or therapeutic functional nanocarriers or molecules in drug-delivery systems may find its main application in the biomedical sector. This work will show the design, synthesis and chemical-physical characterization of multifunctional hybrid materials and nanocomposites, useful for functionalization of textile fabrics and for potential applications in the field of environmentally friendly and sustainable advanced materials.

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Hyper Cross - Linked Polymers as additives for preventing aging of PIM1 membranes

Federico Begni[1], Elsa Lasseuguette[2], Geo Paul[1], Chiara Bisio[1,3], Leonardo Marchese[1], Giorgio Gatti[1], and Maria-Chiara Ferrari[2]

[1] Dipartimento di Scienze e Innovazione Tecnologica, Università degli Studi del Piemonte Orientale" Amedeo Avogadro", Viale Teresa Michel 11, 15121-Alessandria (Italy);[2] School of Engineering, University of Edinburgh, Robert Stevenson Road, EH9 3FB, Edinburgh, (UK)[3] CNR-SCITEC Istituto di Scienze e Tecnologie Chimiche "G. Natta", Via C. Golgi 19, 20133-Milano (Italy).

Polymers of Intrinsic Microporosities (PIMs) can be processed into porous membranes for gas separation applications[1] thanks to the presence of fractional free volume (FFV). However, the FFV of PIM1 tends to be shortlived, soon collapsing to leave fewer transport pathways and reduced gas permeability, a phenomenon called physical aging[2]. One way to address this problem is the insertion within the PIM matrix of porous materials as fillers, thus resulting in Mixed Matrix Membranes (MMMs)[3]. Here we report the synthesis based on the Friedel-Crafts alkylation reaction of two novel porous hyper cross – linked polymer (HCPs) and their employment as fillers for the production of MMMs. The HCPs are obtained from the monomer tetraphenyl methane and the cross – linker tris - bromomethyl benzene and named ABT. According to the temperature and the solvent used in the synthetic procedure (dichloromethane (DCM) for ABT01 or dichloroethane (DCE) for ABT02), two different particles sizes have been obtained, ≈ 500 nm with DCM and ≈ 100 nm or less for DCE. The change in the reaction conditions results in modulation of the surface area and pore volumes. MMMs based on these 2 HCPs and PIM1 have been obtained with a 3% and 10% wt loading and their permeation performances have been studied over the course of more than two years in order to explore physical aging effects over time. Pure PIM1 exhibits the classical aging behaviour of polymers of intrinsic microporosity, namely a progressive decline in gas permeation, up to 85% for the CO_2 permeability[4]. On the contrary, with HCPs, the physical aging at longer times in PIM1 is moderated with a decrease of 60% for the CO_2 permeability. ^{13}C spin-lattice relaxation times (T1) indicates that this slowdown is related to the interactions between HCPs and PIM1.

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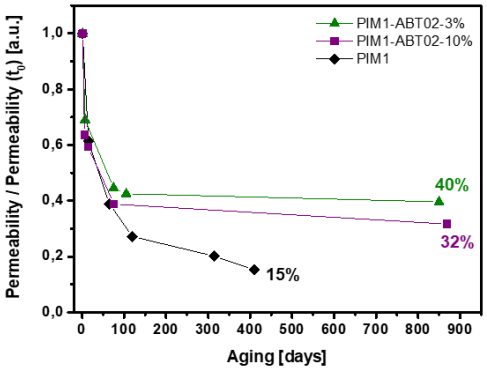

Figure 1. Normalized CO_2 permeation data over time of pure PIM1 and MMMs PIM1-ABT02-3% and PIM1-ABT02-10%.

WO_3-$BiVO_4$ heterojunction: effects of WO_3 nanostructuring on the photoelectrochemical performance

Chiara Nomellini[1], *Annalisa Polo*[1], *Gianluigi Marra*[2], *Maria Vittoria Dozzi*[1], *Elena Selli*[1]

[1] *Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy.*
[2] *Istituto ENI Donegani, Via Fauser 4, 28100 Novara, Italy.*

Nanostructured metal oxide arrays are characterized by large surface areas which can contribute to shorten the diffusion path of photogenerated holes, thus mitigating electron-hole recombination and offering great promise as photoelectrode materials for photoelectrochemical (PEC) hydrogen generation [1]. Indeed, heterojunction nanoarchitectures can increase both the light harvesting efficiency and the separation of photogenerated charge carriers.

In this work, a nanostructured WO_3 photoanode has been prepared by growing nanoflake-like tungsten oxide arrays (NF WO_3) onto a conductive glass substrate, up to an overall 1 µm thick electrode. $BiVO_4$ was then deposited on NF WO_3 from a precursor solution to obtain a WO_3-$BiVO_4$ composite. WO_3 and WO_3-$BiVO_4$ electrodes with a flat morphology and the same tungsten oxide thickness were also prepared, in order to investigate the effects of WO_3 nanostructuring on the PEC performance of the photoanodes. Linear Sweep Voltammetry analyses evidenced that the flat WO_3 electrode displays a higher photocurrent with respect to the nanostructured one, probably due to the presence of fewer surface defects which hinder the transport of photogenerated holes in NF WO_3 [2]. On the contrary, upon deposition of $BiVO_4$ the nanostructured WO_3-$BiVO_4$ composite shows a considerably higher photocurrent (1.3 mA cm^{-2} at 1.23 V vs RHE) compared to the flat heterojunction (0.4 mA cm^{-2} at the same potential). Moreover, Incident Photon to Current Efficiency analyses (Fig. 1a) evidence that the flat heterojunction exhibits low PEC efficiency below 420 nm, which progressively decreases with decreasing wavelength up to a null IPCE value around 350 nm, due to the activation of a detrimental recombination path [3]. The nanostructured heterojunction, on the other hand, presents growing efficiencies in the UV range and overall higher IPCE values also under visible light. Tests run in the presence of a hole-scavenger containing electrolyte allowed us to calculate the charge separation efficiency η_{sep} in the bulk of the two heterostructures (Fig. 1b), demonstrating that the nanostructured heterojunction photoanode presents a 3-fold higher charge separation efficiency with respect to the flat heterojunction.

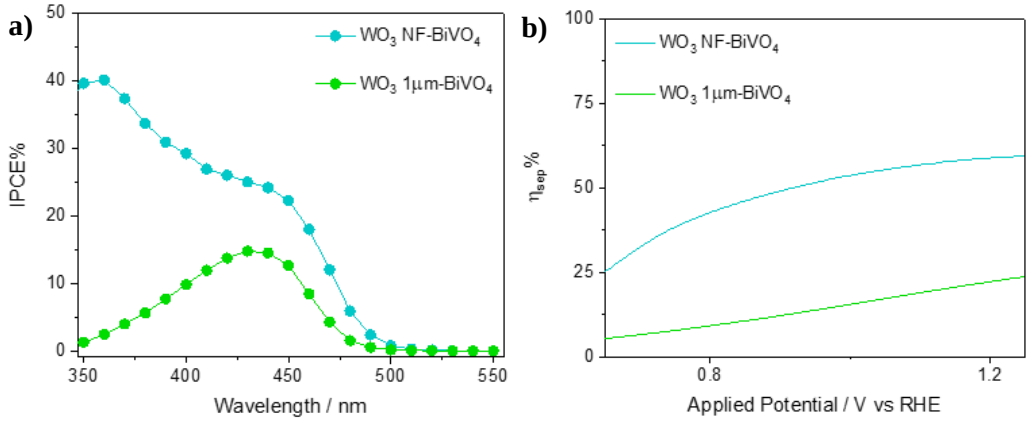

Figure 1. a) back-side Incident Photon to Current Efficiency (IPCE) at 1.23 V vs RHE in 0.5 M Na_2SO_4 and b) charge separation efficiency η_{sep} of the nanostructured (WO_3 NF-$BiVO_4$) and flat (WO_3 1µm-$BiVO_4$) heterojunctions.

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Charge-Transfer Soft Ferroelectrics

Alberto Girlando[a]

[a] *Molecular Materials Group, Strada Fontanini 68, 43124 Parma, Italy*

The quest for organic, or 'soft' ferroelectrics, although crowned by considerable successes [1], continue to be at the focus by intensive research, especially after the discovery of electronic ferroelectricity in low-dimensional Charge-Transfer (CT) crystals [1,2]. The polar nature of ferroelectricity requires that the crystal structure does not have an inversion center, and in CT crystals this amounts to have no inversion center between the molecules and on the molecules. The latter requirement is built-in in mixed stack (ms) CT crystals. In addition, electronic ferroelectricity requires high polarizability, hence intermediate ionicity, as in the case of the low-temperature (< 80 K) phase of TTF-CA [2].

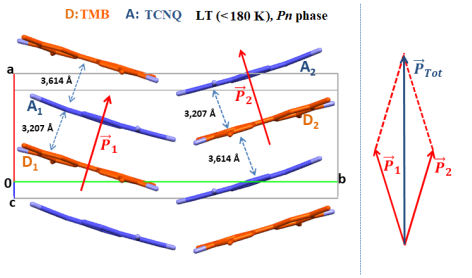

Fig. 1. Structure of the LT phase of TMB-TCNQ

TMB-TCNQ undergoes a first-order valence instability around 180 K. The stack dimerizes and the ionicity is around 0.4. The LT space group is *Pn* with two dimers per unit cell, arranged ferroelectrically [3]. The transition temperature is about 100 K higher than TTF-CA, but in TTF-CA the transition is first order close to second order, whereas in TMB-TCNQ we have a purely first order transition, with 40 K hysteresis. The crystal cracks at the transition since, as shown in Fig.1, when the stacks dimerize the molecules tilt around the *c* axis, so the *a* stack axis increases and the *b* one decreases, causing strain in the crystal.

Another interesting system is M_2P-TCNQ. Here, the stacks are dimerized and the structure is polar already at ambient temperature (*Cm* space group). Moreover, the lattice is highly polarizable, with intermediate ionicity of about 0.5, making M_2P-TCNQ an ideal candidate for electronic ferroelectricity [4]. However, the ferroelectric hysteresis curve was not observed, but rather the typical dielectric signature of a relaxor ferroelectric (Fig. 2). Furthermore, an unusual asymmetric positive-up-negative-down behavior seems to suggest the beginning of polarization switching, but increasing the electric field yields crystal breaking. Polarization reversal in this crystal implies flipping of the bent conformation of the M_2P molecule with an associated energy barrier difficult or impossible to overcome. Evidence of strong electron-phonon coupling suggests that while the polarization is mostly of electronic origin, its possible reversal implies slow collective motions, affected by solid-state intermolecular interactions.

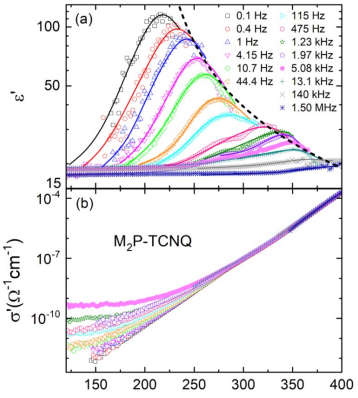

Fig. 2. (a) T dependence of the real part of M_2P-TCNQ dielectric constant; (b) T dependence of conductivity.

From the above examples the importance of weak inter-stack interactions in determining the dielectric behavior and phase transitions of CT crystals is underlined. Understanding and controlling these interactions is required for a proper engineering of effective soft ferroelectrics.

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Designing Spinel Ferrite-Based Nano-Heterostructures Through Versatile Solvothermal Approaches

Marco Sanna Angotzi,[a,b] Valentina Mameli,[a,b] Claudio Cara,[a,b] Anna Musinu,[a,b] Daniel Niznansky,[c] Huolin Xin,[d] Jana Vejpravova,[c] Claudio Sangregorio,[e,b] Carla Cannas[a]

[a]Department of Chemical and Geological Sciences, University of Cagliari; [b]National Interuniversity Consortium of Materials Science and Technology, [c]Department of Inorganic Chemistry, Charles University; [d]Department of Physics and Astronomy, University of California; [e]Italian National Council for Research - Institute for the Chemistry of OrganoMetallic Compounds

Spinel ferrite-based nano-heterostructures (NHSs) have attracted considerable interest in the last decades, thanks to the possibility of joining in a single material magnetic and other physical-chemical properties. Indeed, spinel ferrites represent a class of ferrimagnetic materials widely studied thanks to the chemical and mechanical stability and the possibility to tune the hard or soft magnetic behavior by changing the type of the divalent cation. Furthermore, noble metals (*e.g.*, Ag, Au) have numerous properties (optic, catalytic, antibacterial) that find application in several fields. The most crucial and challenging aspect in designing NHSs is the development of synthesis methodologies able to produce highly crystalline particles having low size dispersity, tunable size, and shape, and defined interfaces. Commonly, the seed-mediated growth approach involves the heterogeneous nucleation of a phase onto pre-existing crystals (seeds), which therefore guides the process. The crystalline structure of the two components (or more in multifunctional NHSs) is the principal constraint for the NHS architecture. Indeed, when iso-structural phases are employed, the coherent epitaxial growth of the second component leads to the formation of well-defined core-shell NHSs,[1–3] with no or small amount of defects and heterojunctions. In contrast, when materials having different crystalline phases react, the growth is generally preferred along a particular direction, generating Janus-, dumbbell-, or flower-like NHSs.[4] Commonly, the seed-mediated growth approach is conducted by the high-temperature decomposition of acetylacetonates in the presence of surfactants. Nevertheless, the necessity of more eco-friendly strategies has moved the interest toward alternative synthetic approaches. In this context, the solvothermal methods feature several advantages, such as the use of low-boiling and inexpensive solvents, the ease of the synthesis, and the possibility to monitor pressure and temperature. Furthermore, the biocompatible oleate molecule has a central role acting as the precursor, the surfactant, and the capping agent, and avoiding the employment of other chemicals and the related compatibility issues. The fine-tuning of different synthetic parameters, such as the temperature, the concentration of precursors, and the type and amount of solvents, allows evidencing the potentiality and versatility of this strategy for the production of well-defined spinel ferrite core-shell nanoparticles and silver-spinel ferrite flower-like NHSs. The combination of hard and soft ferrimagnetic materials with noble metals, featuring localized surface plasmon resonance, can be particularly useful for the magnetic fluid hyperthermia coupled with the photothermal therapy.

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Physico-Chemical Characterization of Polydimethylsiloxane Electrospun Fibers

Stefano Alberti [a], Andrea Dodero [a], Greta Chiocchia [a], Silvia Vicini [a], Maila Castellano [a], Maurizio Ferretti [a]

[a] Department of Chemistry and Industrial Chemistry, University of Genoa, via Dodecaneso 31, 16146, Genova (GE), Italy

The electrospinning process is a relatively recent technique which is now gaining momentum due to its performance. This technique exploits a high electric potential applied between a metallic needle, linked to a syringe, and a metallic collector, to create a solid material out of viscous solutions. When the electric force overcomes the viscous and tension forces, the solution's drop tends to modify into a conical shape, known as Taylor's cone, from which it's possible to withdraw the fibres towards the collector, eventually creating a membrane with a three-dimensional fibrous network in the micro- or nano- scale. The electrospinning process can be easily automated in most of the operating procedures and this can ensure a very good reproducibility and also ease of industrial processing and production. For instance, many parameters can be actually controlled: a) positive and negative potential values, b) the distance between needle/collector, c) the flow rate of the polymeric solution, and d) the relative humidity and temperature. By controlling these parameters, it is possible to control the membrane characteristics, eventually obtaining a tailored product [1]. The possibility of creating thin and solid threads is given by the high viscosity of the polymeric solutions that are introduced in the syringe, as it is the case of polydimethylsiloxane (PDMS), a silicon-based polymer with excellent properties that can undergo crosslinking reactions [2]. PDMS is a choice material because a) it is resistant to temperature and mechanical stress, b) chemically inert to the effect of oxidation, non-soluble for most solvents and resistant against ageing. Eventually, the introduction of the polymeric solution to the electrospinning process has widened the fields of its applications. PDMS properties can be enhanced by creating composite devices, by dispersing materials with different features within the silicon-based solution: PDMS inertness can be exploited to stabilize these materials, preventing their contact with the external atmospheric conditions by embedding them into the polymeric matrix and the resulting device will exhibit the qualities of both. The synthesis of a suitable PDMS polymeric solution as well as the electrospinning procedures are investigated. Resulting fibrous membranes are subjected to an in-depth physico-chemical characterization by means of: FTIR, Contact angle, Rheological and Mechanical Properties, SEM-EDS and TGA-GC-MS, in order to investigate the material's features and eventually to understand its potentiality in the material science field. Some preliminary examples of the PDMS and TiO_2 based coupled system will be presented along with the physico-chemical characterization of the membrane, in order to show one example of the several potential applications: upon irradiation with a proper light source, TiO_2 can exhibit photocatalytic activity that could be exploited for the degradation of pollutants and the deactivation of bacteria colonies. The supporting synthesis of the photocatalyst on the PDMS membrane leads to the formation of antibacterial membranes that can be used in environments with high risk of contamination such as ambulances or operating rooms [3,4].

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C-H terminations in activated carbons and related catalysts:an Inelastic Neutron Scattering spectroscopy and DFT study

Eleonora Vottero[a], Michele Carosso[a], Monica Jimenez Ruiz[b], Riccardo Pellegrini[c], Elena Groppo[a], and Andrea Piovano[b]*

a) Department of Chemistry, NIS Centre and INSTM, University of Turin, Via Pietro Giuria 7, Turin, I-10125, Italy; b) Institut Laue-Langevin (ILL), 71 Avenue des Martyrs, 38042 Grenoble, France; c) Chimet SpA–Catalyst Division, Via di Pescaiola 74, Viciomaggio Arezzo, I-52041, Italy

We present the possibilities provided by the complementary employment of Inelastic Neutron Scattering (INS) spectroscopy and DFT simulations for characterizing the morphology of the C-H terminations in sp^2 carbon materials, focusing on Activated Carbons (ACs) and their modifications upon the deposition of Pt and Pd nanoparticles [1]. INS is a vibrational spectroscopy without selection rules and particularly sensitive to the vibrational modes involving H atoms, which makes this technique able to provide the spectral fingerprint of all the H-containing species in a sample [2-3]. These measurements are generally coupled with DFT simulations on model systems in order to precisely assign the spectral bands [4]. In this work, we focused on four different activated carbons of wood and peat origin physically activated by steam, together with six catalysts prepared by depositing Pt or Pd nanoparticles on these supports. All the samples were prepared and provided by the Catalyst Division of Chimet S.p.A. High-resolution INS spectra of all the samples were collected on the Lagrange instrument at the Institut Laue-Langevin (Grenoble, France).

Significant differences are present in the INS spectra of the four ACs, and evident modifications are observed when the INS spectra of the catalysts are compared to that of the correspondent parent support (Figure 1A). The changes in the relative intensity of the three bands indicate that not all the C-H terminations are affected to the same extent. In order to interpret such differences, we performed a systematic DFT analysis on aromatic models. In this way, it was possible to obtain the INS fingerprints of several regular and defective C-H terminal geometries, which were fitted to the experimental spectra to retrieve their concentrations in the sample (Figure 1B). Our results show that the most frequent C-H terminations in ACs are constituted by benzene rings exposing one or two adjacent H atoms in hexagonal geometries, in different ratios depending on the AC sample. Disordered terminations and physical defects are also necessary to complete the description. The decrease in the catalysts' spectra intensity is mostly attributed to a drop in the concentration of benzene rings exposing a single C-H group, indicating that these terminations are the most affected by the interaction with the metal phase.

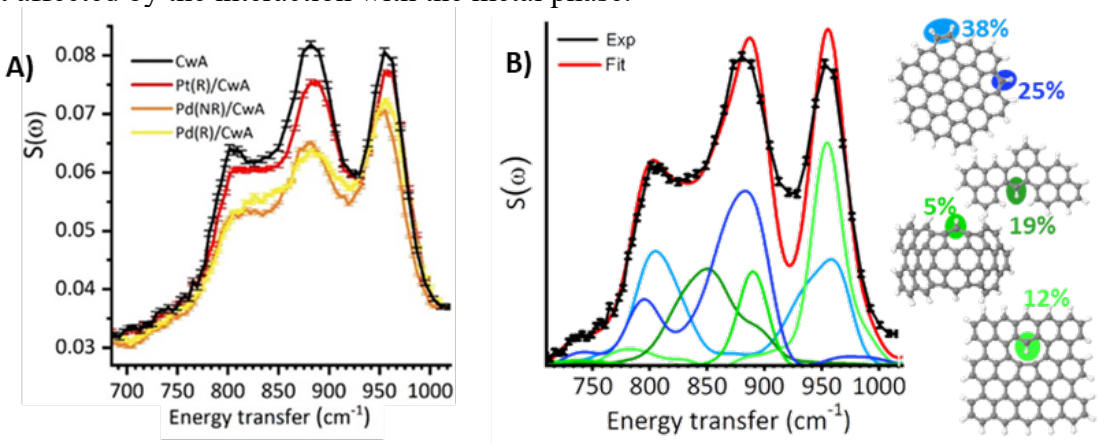

Figure 1: Part A: INS spectrum of an AC of wood origin (black) compared to those of three catalysts obtained by depositing Pt or Pd nanoparticles on it (red, orange and yellow). Part B) Result of the linear combination fit analysis. On the right, the terminal C-H geometries considered and their relative percentage in the final solution are reported.

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Structural Characterization of Deep Eutectic Solvents Mixtures with Water and Methanol

Matteo Busato, Alessandra Del Giudice, Valerio Di Lisio, Pierpaolo Tomai, Valentina Migliorati, Alessandra Gentili, Andrea Martinelli and Paola D'Angelo[a]

[a] *Dipartimento di Chimica, Università di Roma "La Sapienza", P.le A.Moro 5, 00185 Roma, Italy*

Deep eutectic solvents (DESs) are gaining increasing attention as a more sustainable alternative to traditional solvents for several applications. DESs are formed by the combination of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) that liquefy upon contact producing a eutectic with a melting point significantly lower than those of the starting materials. The eco-friendliness and the wide-ranging application horizon of these solvents are guaranteed by their negligible vapor pressure, non-flammability, high conductivity, high solvation capabilities, and low toxicity [1].

Besides the study of "pure" DESs, interest has recently been devoted to DESs mixtures formed upon co-solvent addition. Indeed, the addition of molecular solvents like water, alcohols, or alkanes, has been shown to dramatically affect several DESs physico-chemical properties, eventually providing eutectics with enhanced performances and lower costs.

Here we present a study about the structural characterization of some DESs and of their mixtures obtained upon addition of water and methanol (MeOH) as co-solvents. Small- and wide-angle X-ray scattering (SWAXS), ATR-FTIR spectroscopy and molecular dynamics (MD) simulations have been employed to study the changes in the nanostructure of the archetypal DES "reline" (choline chloride (ChCl):urea 1:2) and of the eutectic formed by ChCl and sesamol in 1:3 ratio [2] upon co-solvent addition. For high water contents, segregation between sesamol- and water-rich regions occurs for the ChCl:sesamol 1:3 DES, up to the formation of water pores able to confine most of the ChCl and disrupt the DES internal structure, while not provoking macroscopic phase-separation [3]. Differently, segregation was not displayed by the reline DES and by MeOH mixtures. The formation of such pseudo-phase aggregation has important implications in light of the applicative conditions of these DESs in liquid-liquid microextractions [4]. The obtained fundamental insights provided knowledge about the link between the structural arrangement of these systems and their macroscopic physical-chemical properties, being a step forward in the development of DESs as advanced processing media for sustainable applications.

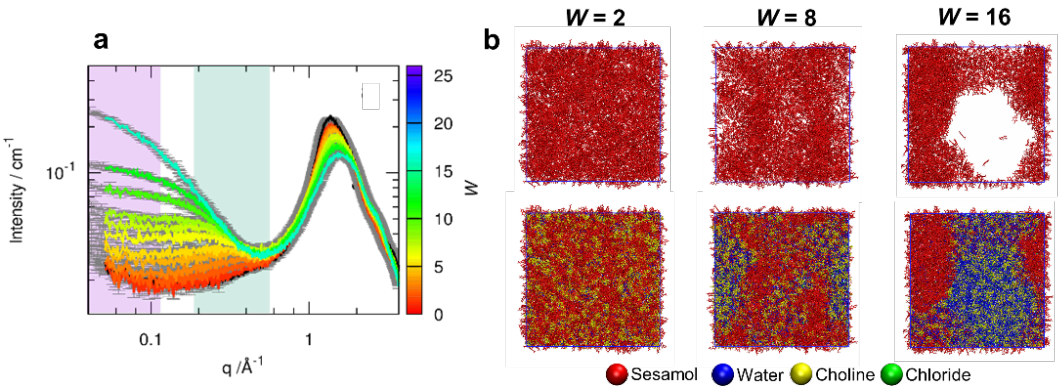

Figure 1. a) SWAXS and b) MD characterization of water:ChCl:sesamol mixtures at different *W*:1:3 molar ratios.

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Use of REOBs and industrial by-products additives for new bitumen-like material formulation: chemical physical and mechanical characterization

Michele Porto[1], Valeria Loise[1], Paolino Caputo[1], Abraham A. Abe[1], Cesare Oliviero Rossi[1]*

[1]Department of Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Cubo 14/D, Rende (CS) 87036, Italy;

An ever-increasing pressure on resources and environmental protection, especially in CO_2 reduction [1], lead to "a systemic change in the use and recovery of resources in the economy" through a clearly transition to a regenerative circular economy [2,3] by creating a close-loop system, minimizing the use of resource inputs and the creation of wastes, pollution and carbon emissions [3]. Therefore, a new potential pathway in innovation and investment, eliminating wastes and the continual use of resources has been proposed. From this perspective the reuse of an opportunely re-refined end of life oils from automotive industry, [4,5] that have become unfit for the use for which they were originally intended, produced by the Itelyum Regeneration srl [6] completely fulfil the Circular Economy goals. By using a refining technology called Revivoil the company can produce, through a final treatment with a catalytic hydrogenation at high pressure, named as Hydrofinishing, three different types of refined high value base oils with API Group II characteristics [4,5], gasoil and a less valuable bitumen product (marketed as Viscoflex 1000® and Viscoflex 2000®). Nowadays, the latter is used mainly as a bitumen additive or bituminous membrane production. However, in the view of a circular economy and considering the opportunity to reduce as much as possible the crude oil extraction, an interesting project has been started between Universities and industries aimed to increase the Viscoflex properties by using additives (chemical e/o natural). Moreover, the additives themselves derive from other waste sources (e.g. end of life tyres, waste papers, etc.) and produce a new higher performing bituminous binder [7] with flexible and specific applications by tuning rheological and mechanical properties to satisfy the Italian National requirements and or International ones and to be employed directly in asphalt mixtures production.

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Chitosan covalently functionalized with peptides mapped on Vitronectin and BMP-2 for bone tissue engineering

A. Zamuner[a], P. Brun[b], G. Iucci[c], G. D'Auria[d], L. Cassari[a], M. Dettin[a]

[a] Department of Industrial Engineering, University of Padua; [b] Department of Molecular Medicine, University of Padua; [c]Department of Sciences, University Roma Tre; [d]Department of Pharmaceutical Sciences, University Federico II of Naples.

Next generation biomaterials are called to improve specific interactions with the cellular component of the tissue to be repaired or regenerate. For this aim, we have functionalized the natural biopolymer chitosan [1] with two bioactive peptides: an adhesive sequence patterned on Human Vitronectin (HVP) [2] and a sequence of Bone Morphogenetic Protein 2 (BMP-2) [3] able to induce cellular differentiation toward the osteoblastic phenotype. The conjugation involved the amino groups of chitosan and an aldehyde group appositely inserted in peptide sequences and it was followed by a reduction of Schiff bases. The novel biomaterials were characterized by SEM, FT-IR, NMR, and XPS. The scaffolds produced through lyophilization were seeded with human osteoblasts: the adhesion, the proliferation, and the calcium deposition resulted improved in comparison with the control (plain chitosan). In addition, the genic expression of three important proteins (RUNX2, Vitronectin and Osteopontin) resulted significantly increased with respect to the control.

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Study of the bioactivity of thin glass-ceramic films deposited on electrospun polymeric scaffolds by nanosecond PLD

A. De Bonis[a] , M. Curcio[a], , A. Pepe[a], B. Bochicchio[a], A. Laezza[a], R. Teghil[a] J. V. Rau[b]

[a]Dipartimento di Scienze, Università della Basilicata,Viale dell'Ateneo Lucano, 10 -85100 Potenza – Italy [b] Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche (ISM-CNR), Via del Fosso del Cavaliere, 100-00133 Rome, Italy

In the last years there were significant advances in the development of new technologies to meet the demand for low cost biomedical materials. We have conjugated two methodologies that were emerged as powerful approaches for tissue engineering application: electrospinning to fabricate a nanofibrous polymeric scaffold and Pulsed Laser Ablation to tune and control the composition and morphology of the exposed surface. A multicomponent scaffold composed of synthetic and natural polymers has been proposed to join the good biocompatibility, biodegradation and good mechanical properties of poly (D,L- lactic acid) (PDLLA) and the hydrophilicity and cellular affinity of gelatin (GE). In the frame of a biomimetic strategy for the generation of multifunctional scaffolds, we have coated the electrospun fibers with a thin film of an inorganic bioactive glass supplemented with manganese ions. The nanosecond laser ablation and deposition mechanisms of the glass were studied by *in situ* and *ex situ* techniques. The properties and composition of the bilayered scaffold were investigated and its bioactivity in terms of induced mineralization was tested by incubation in simulated body fluid (SBF) buffer. The kinetics of the inorganic film dissolution and the calcium phosphate phases growth were followed by microscopic and spectroscopic techniques, confirming that a combination of bioactive glass-ceramics and nanofibrous scaffolds holds promising potential for inducing mineralization in connective tissues.

Crystallization of amorphous calcium phosphate to hydroxyapatite nanoparticles: new insights in the field of biomaterials and biomineralization

Michele Iafisco

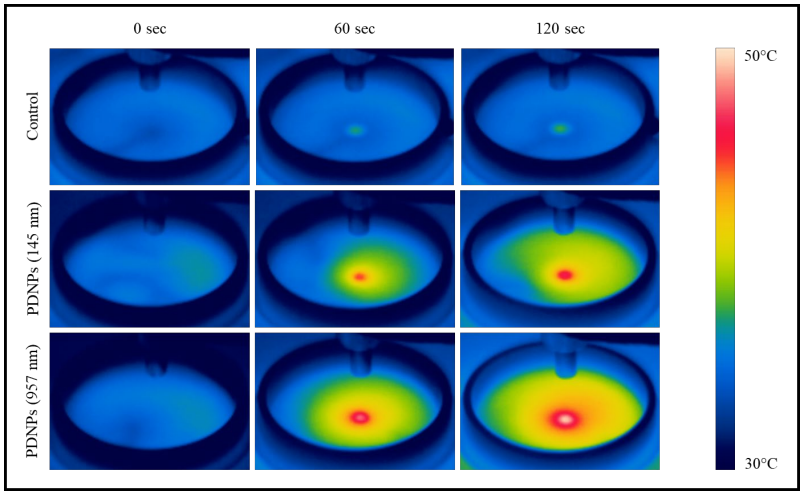
Laboratory of Bioceramics and Bio-hybrid Composites, Institute of Science and Technology for Ceramics, ISTEC-CNR, Faenza, Italy

Study of the impact of size on the properties of polydopamine nanoparticles and their interaction with glioblastoma multiforme cells

Alessio Carmignani[a,b], Matteo Battaglini[a], Gianni Ciofani[a]

[a] Istituto Italiano di Tecnologia, Smart Bio-Interfaces, Viale Rinaldo Piaggio 34, 56025 Pontedera (Pisa), Italy[b] Scuola Superiore Sant'Anna, The Biorobotics Institute, Viale Rinaldo Piaggio 34, 56025 Pontedera (Pisa), Italy

Polydopamine nanoparticles (PDNPs), thanks to their structure, shows unique properties that have attracted attention in the biomedical field, such as antioxidant activities and near-infrared (NIR) photo-thermal conversion abilities.[1,2] These organic structures, in addition of being exploited in materials sciences, are also widely exploited in the field of cell biology owing to the possibility to be fully degraded in a physiological environment, avoiding the formation of potentially harmful accumulation inside cells.[2]
In this study, we evaluated how these properties change as the size of the nanoparticles (NPs) varies. Using a Stöber reaction protocol and changing ratios between reagents, we obtained PDNPs of 8 different sizes, from 145±13 nm to 957±49 nm. After a preliminary characterization in terms of size, surface charge, morphology, and NIR absorption, we focused on antioxidant capacities, NIR photo-thermal conversion abilities, and interaction with glioblastoma multiforme cells in terms of cellular internalization.
Results show that by increasing the diameter, an increment of the NIR absorption occurs, that leads to an increment of the photo-thermal conversion abilities (Figure 1). Conversely, by decreasing the size we observed an increment of the antioxidant capacities and an increment of the cellular uptake by glioblastoma multiforme cells.
The data collected from these experiments highlighted how size is an essential aspect to be taken into consideration in the choice of the most suitable nanovector for biomedical applications.



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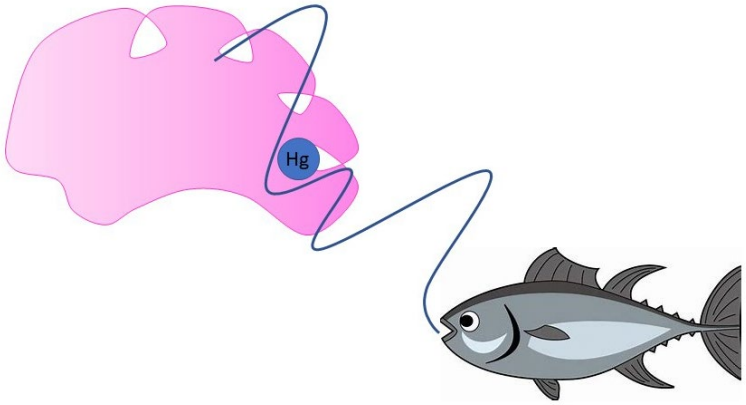
Methylmercury toxicity: insight from a theoretical physical-chemical description

Laura Orian, Andrea Madabeni

Dip. Scienze Chimiche Università degli Studi di Padova Via Marzolo 1 35129 Padova

The toxicity of methylmercury (CH_3Hg^+), a hazardous neurotoxicant found in the environment and in food, is a great concern for WHO, which has included mercury in the list of the ten most dangerous substances. While the environmental aspects of mercury pollution are well known, its toxicological mechanisms are still unclear. The most plausible hypothesis is that its targets are the cysteines (Cys) and selenocysteines (Sec) of important enzymes like thioredoxin reductase (TrxR) and glutathione peroxidase (GPx), both involved in the complex endogenous defense system against oxidative damage and in redox signalling. The inhibition of these thiol/selenol based proteins likely starts with the formation of a mercury-chalcogen bond. Experimental evidence of the formation of Se-Hg bond in thioredoxin reductase has been reported only very recently. [1]



In our seminal studies, fully carried out *in silico* using state-of-the-art validated computational methods, we present and discuss (i) model Rabenstein's ligand exchange reactions involving a methylchalcogenolate and a methylmercurymethylchalcogenide as substrate, which represent the archetypal processes through which, when S or Se are involved, CH_3Hg^+ can be distributed in the organism; [2] (ii) the effect of methylmercury binding on the oxidation of a Cys/Sec by H_2O_2; in fact, the reduction of the hydroperoxides is a very common elementary step in redox biology, typically performed by a Cys or a Sec residue. Particularly, this toxicological/bio-inorganic problem is addressed: can the Cys/Sec residue still reduce H_2O_2 after mercury-chalcogen bond is formed? [3] (iii) a possible mechanism of toxicity focusing on the hypothesis that, in presence of H_2O_2, selenium is first oxidized and then undergoes an elimination reaction leading to the formation of dehydroalanine (Dha), which irreversibly impairs the enzymatic function. Our outcomes prompt for novel experiments on model molecular as well as on biological systems.

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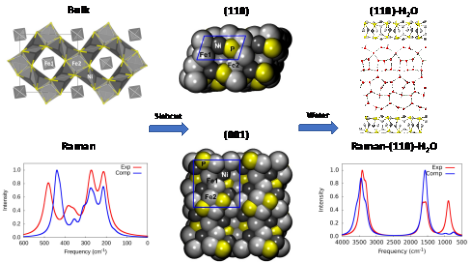
Ab-initio modelling of Fe_2NiP-H_2O interaction: a phosphate factory for Early Earth

Marta Corno[a], Stefano Pantaleone[a,b], Nadia Balucani[b,d,e], Albert Rimola[c], Piero Ugliengo[a]

[a] Dipartimento di Chimica and Nanostructured Interfaces and Surfaces (NIS) Centre, Università degli Studi di Torino, via P. Giuria 7, I-10125, Torino, Italy; [b] Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto 8, I-06123 Perugia, Italy; [c] Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain; [d] Osservatorio Astrofisico di Arcetri, Largo E. Fermi 5, I-50125 Firenze, Italy; [e]Université Grenoble Alpes, CNRS, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG), F-38000 Grenoble, France

Phosphorus is ubiquitous in planet Earth and plays a fundamental role in all living systems. Finding a reasonable prebiotic source of phosphorus is not trivial, as common sources where it is present nowadays are in the form of phosphate minerals, which are rather insoluble and non-reactive materials, and, accordingly, unavailable for being readily incorporated in living organisms [1]. A possible source of phosphorus is from the exogenous meteoritic bombardment and, in particular, in iron/nickel phosphides [3,4,5]. These materials, by simple interaction with water, produce oxygenated phosphorus compounds, which can easily react with organic molecules, thus forming C-O-P bonds [6,7]. It has been estimated that up to 10% of the early Earth crust was composed by phosphide minerals, after the heavy meteor bombardment, and that many tons per year of phosphorus oxygenated compounds have been produced [8]. In the present work, periodic ab-initio simulations at PBE level (inclusive of dispersive interactions) have been carried out on Fe_2NiP-schreibersite, as a relative abundant component of metallic meteorites, in order to characterize structural, energetics and vibrational properties of both bulk and surfaces of this material [9]. Moreover, also the interaction with water was analyzed, modelling both high and low coverage regimes, in order to study the corrosion process which ultimately leads to the production of phosphorus oxygenated compounds, like phosphites (HPO_3^{2-}/$H_2PO_3^-$) and phosphates (HPO_4^{2-}/$H_2PO_4^-$).



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First-principles study of the C/Si interface: the influence of graphene corrugation on the H adsorption and abstraction reactions

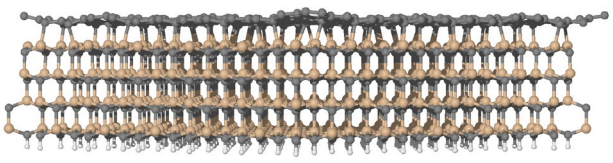
Mirko Leccese[a], Didier Lemoine[b], Rocco Martinazzo[a]

[a]Department of Chemistry, Università degli Studi di Milano, Italy; [b]Laboratoire Collisions Agrégats Réactivité, Université Toulouse III – Paul Sabatier, France

The C/Si interface has drawn an ever-increasing interest in the last years because of its peculiar features that make it appealing from both a fundamental and applied perspective. Such interface consists of two carbon layers grown on the SiC(0001) surface - a "buffer", which is strongly bound to the substrate, and a "graphene" layer, which is in turn only weakly bound to the buffer layer[1]. Hydrogenation of the buffer layer is particularly attractive since it completely decouples the graphene layer, thereby making the latter really free-standing. Furthermore, the corrugation of the buffer layer, which is due to a different strength of the C-Si interactions across the lattice, has shown to have a considerable effect on the energetics of the hydrogen adsorption, that combined with the known flexibility of graphene makes the C/Si interface a possible candidate for a new generation of hydrogen storage devices[2].

The passivation of the buffer layer that lies at the heart of the aforementioned decoupling strategy is ruled by the competition between the adsorption of H atoms and the reactivity of adsorbed species towards abstraction processes, *i.e.* the reaction between an adsorbed H and a gas-phase H that produces molecular hydrogen. In the latter case, the so-called Eley-Rideal recombination, the reaction is barrier-less, and the rate is governed to a large extent by its exothermicity.

At present, modeling of the substrate and the H adsorption energetics has been limited to small-sized systems with a limited ability to accommodate the long-range features of the substrate (its curvature) and of the surface reconstruction that takes place upon adsorption[3]. Here we present a combined energetic and dynamical investigation of the hydrogenation of the buffer layer**.** DFT calculations were performed on the **(**minimal) structure comprising 1310 atoms that is known to describe the observed reconstruction of the clean buffer surface**.** We scrutinized the H adsorption energetics on the buffer layer and related it to the local geometry of the surface around the binding site. Next, we investigated the Eley-Rideal reaction on a number of representative sites of the buffer-layer using a fully quantum approach (a time-dependent wave-packet method[4,5]) within the rigid, flat surface approximation to assess the role of hydrogen adsorption site on the rate (cross-section) of the abstraction process.



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Excited-state symmetry breaking in an aza-nanographene dye

Brunella Bardi[a], Maciej Krzeszewski[b], Daniel T. Gryko[b], Anna Painelli[a], Francesca Terenziani[a]

[a] Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parco Area delle Scienze 17/a, 43124 Parma (Italy); [b]Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44-52, 01-224 Warsaw (Poland)

Symmetry breaking phenomena are widely investigated in quadrupolar chromophores, a large family of charge-transfer (CT) dyes in which an electron donor, D (or acceptor, A) moiety is symmetrically conjugated to two electron withdrawing (or electron-donating) groups, in a ADA (or DAD) architecture[1]. Quadrupolar dyes with a low degree of CT in the ground-state typically undergo symmetry-breaking of the first excited state, which is responsible for sizeable solvatochromic shifts in emission. In this contribution, we demonstrated the occurrence of excited-state symmetry breaking in a structurally unique aza-nanographene dye in which a pyrrolo[3,2-*b*]pyrrole is expanded with fused aromatic rings, yielding a butterfly-shaped structure existing in different double-helical conformations (Figure 1)[2]. The spectroscopic characterization and the computational investigation through complementary theoretical frameworks, DFT and essential-state models, provided an in-depth insight into the complex and unique excited-state scenario of this system, unravelling an underlying quadrupolar-like structure originating from the significant charge-polarization induced by the electron-rich core, in spite of the lack of well-identified A groups[3]. The overlapping between CT states responsible for solvatochromism with intense localized transitions with different polarization introduces new perspectives in the design and application of heterocyclic nanographenes.

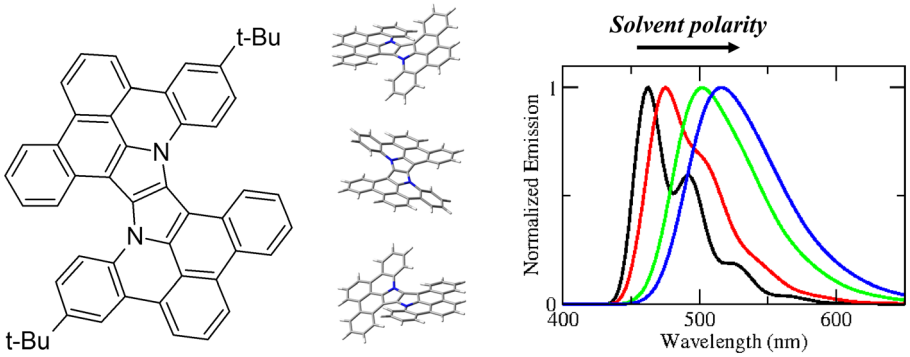

Figure 1. Molecular structure of the aza-nanographene dye (left) and its conformational isomers (middle). The sizeable emission solvatochromism of this dye was rationalized and reproduced adopting an essential-state approach (right).

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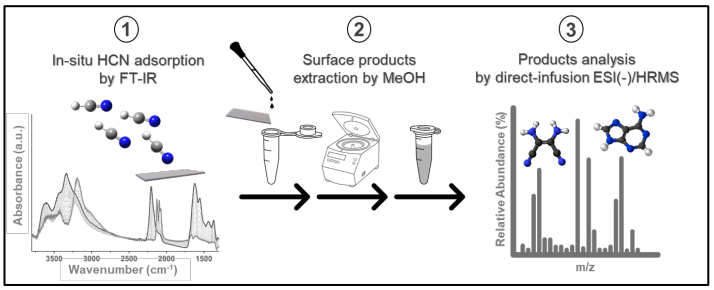
HCN adsorption and reactivity at the Mg_2SiO_4 surface:a laboratory model of the chemistry on interstellar dust grains

Santalucia R.[a], Mino L.[a], Signorile M.[a], Bonino F.[a], Ugliengo P.[a], Scarano D.[a], and Spoto G.[a]

[a] *Department of Chemistry, University of Torino, via P. Giuria 7, 10125, Torino, Italy*

The heterogeneous chemistry of HCN is of great interest in the fields of astrobiology and prebiotic chemistry as this molecule is considered a key precursor in the formation of biomolecules like nucleobases.
In this respect, most of the available literature concerns the HCN reactivity in aqueous systems[1]. On the contrary significant experimental studies devoted to the interaction of gaseous HCN with solid surfaces are lacking, probably because of the security issues related to the production and use of this gas in standard laboratories.
The recent discovery of the presence of complex organic molecules (iCOMs) in the interstellar medium (ISM) have strengthened the idea of an exogeneous origin of prebiotic matter. Indeed, in this scenario the investigation of the interaction of gaseous HCN and its derivatives (which are abundantly present in the ISM)[2] on solids surfaces (like those of ice, silica, silicates, and other minerals forming the interstellar dust) can become relevant for understanding the formation mechanisms of iCOMs and more complex biomonomers containing nitrogen[3].
This work aims to contribute to the field by studying the adsorption and reactivity of gaseous HCN (produced *in situ* under controlled and safe conditions) at the surface of amorphous (AMS) and crystalline Mg_2SiO_4 (forsterite), which are known to be main constituents of the dust grain cores in the ISM and in protoplanetary disks, comets, meteorites, asteroid and protostars[4]. In order to better evaluate the role of the Mg_2SiO_4 surface acidity and basicity in the HCN activation and reactivity, a parallel investigation was performed by using SiO_2 and MgO as simple reference solids.
The experimental workflow is sketched in the Figure. In all cases, the HCN adsorption and reactivity were studied by in-situ FT-IR as a function of the temperature (100-298 K) and of the contact time. The composition of the reaction products was then investigated, after extraction with methanol, by direct-infusion HR-MS.



The experimental results allow to conclude that the Lewis surface basicity due to the coordinatively unsaturated O^{2-} sites present on MgO and Mg_2SiO_4 are responsible of a complex surface chemistry leading to a mixture of N-containing heterocyclic compounds including adenine nucleobase.
These results show that prebiotic molecules can be easily and spontaneously formed on the surface of active solids like Mg-silicates by HCN even in the mild conditions adopted here (low HCN equilibrium pressure, low temperature, absence of external energy sources like UV irradiation or electrical discharges), and further support the possible central role of HCN in the chemistry of life.

[1] M. Ruiz-Bermejo, M. P. Zorzano and S. Osuna-Esteban, *Life* **2013**, *3*, 421-448.
[2] C. N. Matthews and R. D. Minard, *Faraday Discuss.* **2006**, *133*, 393-401; discussion 427-352.
[3] E. Herbst and E. F. van Dishoeck, *Annu. Rev. Astron. Astrophys.* **2009**, *47*, 427-480.
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High value-added mesostructured silica from hexafluorosilicic acid (FSA): from a hazardous waste to precious silicon source.

Claudio Cara,[a, b] Mirko Antonio Vacca, Valentina Mameli,[a, b] Marco Sanna Angotzi,[a, b] Mariano Andrea Scorciapino,[a, b] Maria Giorgia Cutrufello,[a, b] Vaclav Tyrpekl,[c] Luca Pala,[d] and Carla Cannas [a,b]

[a] *University of Cagliari, Department of Chemical Science, Cittadella Universitaria S.P. Monserrato Sestu Km 0.700, 09042 Monserrato, Italy;* [b] *Consorzio Interuniversitario Nazionale per La Scienza e Tecnologia Dei Materiali (INSTM), Cagliari Unit, Via Giuseppe Giusti 9, Firenze, 50121, Italy ;*[c] *Charles University in Prague, Department of Inorganic Chemistry, Hlavova 2030/8, 12843, Prague 2, Czech Republic;* [d] *Fluorsid S.p.A, Area Industriale di Cagliari, 2a Strada Macchiareddu, Assemini, 09032, Italy.*

Hexafluorosilicic acid (H_2SiF_6 or FSA), an industrial waste deriving from the fertilizer industry and the production of HF, has been proven to be a low-cost alternative to silicate esters for the synthesis of high-quality MCM-41 (high surface area, high degree of order, narrow pore size distribution, high thermal stability) through a head-to-head comparison between the most common silica precursor, tetraethylorthosilicate (TEOS), and FSA. The effect of different parameters such as temperature, time, hydrothermal treatment, and the presence of ethyl acetate has been explored by studying the textural, structural, and morphological features in order to assess the best experimental conditions for the synthesis of high-quality MCM-41 from FSA. On the most promising samples, thermal and hydrothermal stability has been assessed, indicating a higher thermal stability for the FSA-derived sample, due to the thicker walls, and comparable hydrothermal stability. The mother solution treatment with calcium hydroxide has allowed the obtainment of nanostructured fluorite as an additional valuable product and a CTAB-rich ammonia solution, which can be employed for successive synthesis with FSA. Recovery processes for the templating agent entrapped in the MCM-41 mesostructure by ethanol have also been explored for both FSA- and TEOS-derived samples, showing an easier removal in the case of FSA-MCM-41. Moreover, mesostructured silica derived from FSA has also been proven to be an ideal support to design efficient and regenerable mesostructured iron oxide-based sorbents for H_2S removal from syngas, showing similar performance to that of the corresponding nanocomposite prepared from TEOS. The utilization of a waste as the silicon source and the opportunity to produce CaF_2 and recover ammonia and CTAB may be instrumental in designing an efficient process, abiding by the dictates of both green chemistry and blue economy.[1]

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A sustainable approach to formulation chemistry:structure and dynamics of bio-based complex mixtures

Rodolfo Esposito[a], *Luigi Paduano*[a,b], *Gerardino D'Errico*[a,b]

[a] *Department of Chemical Sciences, University of Naples Federico II, Naples, Italy;* [b] *CSGI, Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase, Italy.*

The well-established circular model of social growth drives chemical industry to minimize wastage and maximize reuse, recycle and remanufacturing (3R). Formulation chemists have focused on the re-design of current products in an ecological perspective. However, the simple replacement of polluting chemicals by more biodegradable ones is not enough. The whole formulation process has to the re-drawn on the basis of compatibility and sustainability criteria.
Nature offers a guiding line for a new concept of formulation eco-design [1,2]. Indeed, during evolution all living organisms have set up intra- and/or extra-cellular complex fluids. The physico-chemical analysis of these fluids in terms of the key concept typical of formulation technology as well as in colloid science reveals unexpected analogies between biological and industrial fluids, showing which are the solutions nature has optimized to solve each functional problem.
Bacteria regulate the properties of the extracellular matrix by releasing finely engineered (macro)molecules. From a physico-chemical viewpoint, exopolysaccharides (EPS) are biopolymers acting as rheology modifiers, optimized to work in specific conditions. Diffusion and micro-rheology measurements show that the conformation of the EPS produced by *Zymomonas mobilis*, an ethanologenic Gram negative bacterium, unlike other polymers, is almost unperturbed in the presence of ethanol [3]. For this reason, it is a perfect component of virucidal and bactericidal ethanol-rich formulations.
At the same time, bacterial biosurfactants effectively replace synthetic surfactants. As an example, rhamnolipids produces by Pseudomonas aeruginosa can be considered, from a physicochemical viewpoint, as di-chained surfactants able to dramatically lower the medium surface tension and to form large micellar aggregates. Being produced by organisms adapted to live in harsh environments, biosurfactants are less sensitive to changes of the solution conditions. Indeed, we found that they are able to micellize at extremely high content of bio-ethanol and bio-glycerol, naturally occurring co-solvents, playing a variety of roles in complex surfactant mixtures. A deep and large physico-chemical characterization of these bio-inspired formulations, based on surface tension, calorimetry and DLS, as well as on electron spin resonance and spectrofluorescence (using appropriate spin-probes) indicates that biosurfactants and EPS act synergistically allowing to finely tune the mixture structural and rheological properties.
Overall, our results demonstrate that complex fluids naturally occurring in biological systems can be profitably used as models of new-generation chemical formulations [4].

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[2] C. Caianiello, L. Paduano and G. D'Errico, *Nanomaterials*, **2020**, *10*, 1185.
[3] M. Pallach, G. D'Errico, A. Silipo, *Carbohydr. Polym.*, **2018**, *201*, 293.
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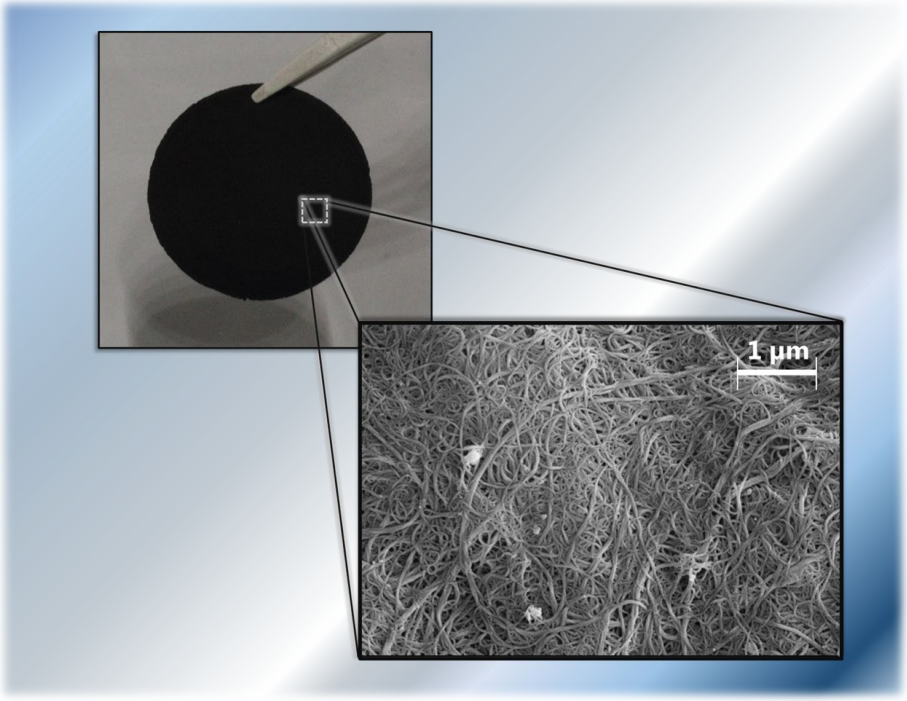
Photocatalytic degradation of organic pollutants in water using an innovative TiO_2/SWNT membrane

Baratta Mariafrancesca[a], De Filpo Giovanni[a], Tursi Antonio[a], Mashin Aleksander I.[b], Nicoletta Fiore P.[c]

[a] Department of Chemistry and Chemical Technologies, University of Calabria, 87036 Rende (CS), Italy; [b] Applied Physics & Microelectronics, Lobachevsky State University of Nizhni Novgorod, 603950 Nizhni Novgorod, Russian; [c] Department of Pharmacy, Health and Nutritional Sciences, University of Calabria, 87036 Rende (CS), Italy.

Carbon nanotubes membranes, better known as buckypapers (BP), have been recently proposed as innovative filtration systems thanks to their mechanical, electronic and thermal properties. TiO_2, WO_3, ZnO semiconductors are common photocatalytic materials, usually used to enhance polymer membranes properties in wastewater treatment, fouling mitigation and permeation. In this work, flexible single walled carbon nanotubes membranes are prepared and characterized by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), flux and conductivity measurements. For application in advanced oxidation processes, a TiO_2 thin layer is deposited on BP surface by electron-beam evaporation and TiO_2 crystalline phase determined by Raman spectroscopy. TiO_2/BP composite membrane photocatalytic efficiency is tested against model pollutants such as Methylen Blue and pesticides in a small continuous flow reactor and compared with the performance of an equivalent homogeneous TiO_2-based reactor.

[1] G. De Filpo, E. Pantuso, A. I. Mashin, M. Baratta, F. P. Nicoletta, *Membranes*, **2020**, *10*, 157.



Plasma deposition of TiO_2-based nanocomposite coating for photocatalytic degradation of organic pollutants in water

C. Lo Porto [a], F. Palumbo [b], M. L. Curri [a, c], R. Comparelli [a]

[a] CNR-IPCF, Istituto per i Processi Chimico-Fisici, S.S. Bari, c/o Dip. Chimica Via Orabona 4, 70126 Bari, Italy;[b] CNR-Nanotech, Istituto di Nanotecnologia, c/o Dip. Chimica Via Orabona 4, 70126 Bari, Italy;[c] Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Via Orabona 4, 70126 Bari, Italy.

Water treatment is a topic of ever-increasing interest in the scientific community due to the relevance of water quality for society and many approaches are investigated to face such a challenge, among them advanced oxidation processes (AOPs) are receiving growing attention. [1-2] Here, this work presents the deposition of photocatalytic nanocomposite coatings based on TiO_2 nanoparticles embedded in an organic matrix deposited on stainless steel mesh. The deposition has been obtained by aerosol assisted atmospheric pressure plasma fed with He and a suspension of TiO_2 nanoparticles in a mixture of hexamethyldisiloxane (HMDSO) and isopropyl alcohol (IPA). This procedure has been already used to deposit TiO_2-based coatings, although the actual photocatalytic activity of the obtained films has been rarely documented. [3-6] The photocatalytic activity of the obtained coatings has been tested under UV light for the degradation in water of methylene blue (MB), used as model molecule. The effect of deposition time of the discharge has been evaluated on the photocatalytic performance of the coatings, Deposition time of 3min (*TiO_2-3m*) and 20min (*TiO_2-20m*) resulted in 36% and 55% MB degradation after 90min irradiation. The possible effect on photocatalytic performance of an O_2 plasma post-treatment *(-P)* on the obtained coating has been also investigated. Interestingly, a further increase in the photocatalytic rate has been observed in both cases, reaching 50% and 63% for *TiO_2-3m-P* and *TiO_2-3m-P,* respectively. The comparison of the degradation % in time is reported in Fig.1A, along with the data recorded for *TiO_2-3m* in the dark, and for the direct photolysis experiment. The effects of longer deposition time and of plasma post-treatment on the chemistry and morphology of the coatings have been also evaluated. The photocatalytic activity of the coatings has been found stable over at least 5 cycles of use.

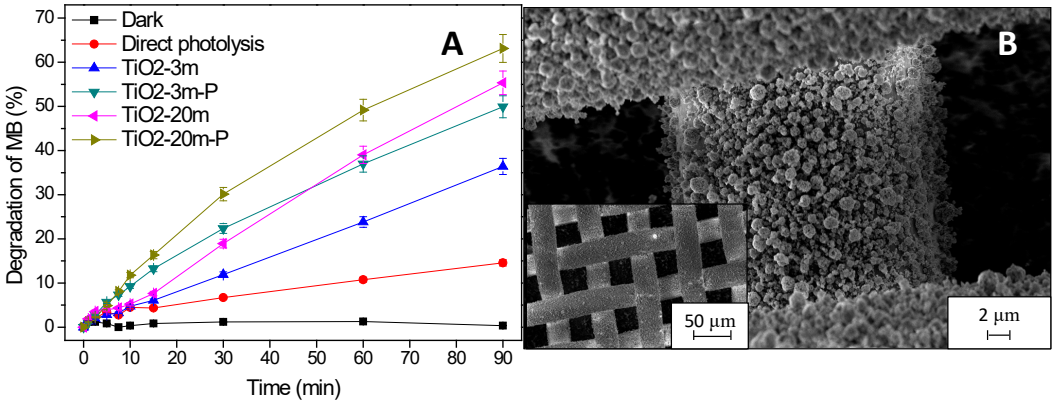


Fig.1 – A) Degradation of methylene blue (MB) by TiO_2-3m, TiO_2-3m-P, TiO_2-20m, TiO_2-20m-P, compared with TiO_2-3m kept at dark and direct photolysis. B) Scanning electron microscopy (SEM) image of the mesh covered with TiO_2-20m coating at 5kx (1kx for the inset) magnification.

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Synthesis and characterization of polydopamine coated SPIONs for Cu^{2+} ions removal of from water

Siciliano Giulia[a], Turco Antonio[b], Fanizza Elisabett [c,d], Comparelli Roberto[d], Curri M. Lucia[c,d], Monteduro Annagrazia[a], Quarta Alessandra[b], Depalo Nicoletta[d] ,Maruccio Giuseppe[a]

[a] Department of Maths and Physics "Ennio De Giorgi", Università del Salento; [b] Institute for Chemical and Physical Processes (IPCF)-CNR SS Bari, Via Orabona 4, 70126 Bari, Italy; [c] Institute of Nanotechnology (NANOTEC)-CNR SS Lecce, Via Monteroni; 73100, Lecce, Italy; [d] Department of Chemistry, University of Bari, Via Orabona 4, 70126 Bari, Italy

The removal of pollutants such heavy metals, aromatic compounds, dyes, pesticides, pharmaceuticals from water is still a challenge. Many methods have been exploited for the purification of water from contaminants including photocatalytic degradation, biological treatment, adsorption, chemical precipitation [1-2]. Absorption based techniques are still considered among the most efficient and used thanks to its easy operation. In recent years, polydopamine coated magnetic nanoparticles have emerged for the uptake of heavy metals in water treatment, since they combine magnetic separation and specific affinity towards pollutants. In this context, this work focuses on the synthesis of polydopamine (PDA) coated Super Paramagnetic Iron Oxide Nanoparticles (PDA@SPIONs) as adsorbent for Cu^{2+} ions, in order to work as functional nanostructures for the collection of Cu^{2+} in water by the application of a magnetic field. The synthetic parameters, including the amount of SPIONs and PDA, have been thoroughly investigated in order to define their effects on the nanostructure morphology and size. Subsequently, as prepared nanostructures have been treated with a Cu^{2+} solution under basic conditions in order to evaluate the PDA ability to bind metal ions. A systematic investigation of the prepared functional nanostructures has been carried out by means of complementary spectroscopic, morphological and magnetic techniques. Inductively coupled plasma mass spectrometry (ICP-MS) measurements have been performed in order to estimate the binding ability of PDA towards Cu^{2+} ions. The investigation of the properties of the nanostructures demonstrates that they hold a great promise for future bioremediation applications.

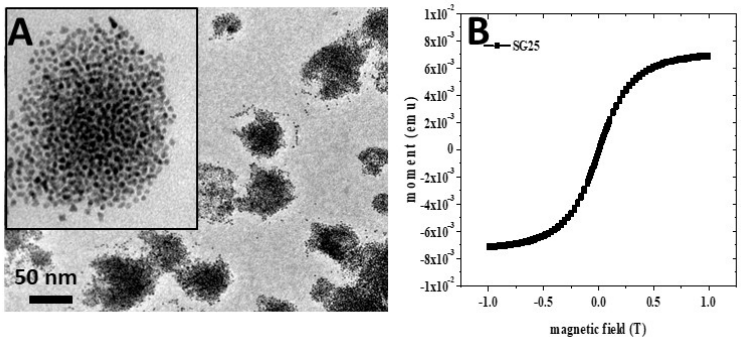

Fig.1: a) TEM images and b) magnetic characterization of the prepared PDA coated SPIONs. Room temperature hysteresis cycle of nanostructures revealed a superparamagnetic behaviour.

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The NMR relaxometry as a powerful tool to study the uptake of paramagnetic ions from water by synthetic saponite clays

S. Marchesi,[a] S. Nascimbene,[a] M. Guidotti,[b] F. Carniato[a] and C. Bisio[a,b]

[a] Dipartimento di Scienze e Innovazione Tecnologica, Università degli Studi del Piemonte Orientale "Amedeo Avogadro", Viale Teresa Michel 11, 15121-Alessandria (Italy); [b] CNR-SCITEC Istituto di Scienze e Tecnologie Chimiche "G. Natta", Via C. Golgi 19, 20133-Milano (Italy)

Transition and rare-earth metals are considered *critical key elements* for the technological evolution of the human society, and they have been extensively used in several economic sectors due to their unique electronic, magnetic, optical and catalytic properties.[1] Undeniably, the recycling of these raw materials is of great importance for several reasons, from reduction of overall usage costs to lessening of the environmental pollution linked to the waste materials containing them. Traditional recovery processes are based on solvent extraction, but requires many steps and large amount of solvents. The development of more sustainable recovery solutions with higher efficiency, lower costs and reduced environmental impact represents an imperative challenge: particularly, solid sorbents have been successfully studied for this purpose. In a previous work, we studied the sequestration of lanthanides (La^{3+}, Gd^{3+}, Lu^{3+}) from aqueous solutions with a synthetic saponite clay, showing promising results if compared to commercial clays[2]. Following those results, we explored further the metal extraction capabilities of synthetic saponite, by experimenting the use of the ^{1}H-NMR relaxometry[3] as a means of simple, fast and effective real-time monitoring tool of the uptake of (paramagnetic) metal ions from water. This has been possible by analysing the longitudinal relaxation rates (R_1 [s^{-1}]) of the ^{1}H of water molecules in the presence of the paramagnetic metal over time, because this parameter can be correlated to the amount on metal captured by the clay. Three paramagnetic ions were tested (Gd^{3+}, Co^{2+}, Cu^{2+}) and a synthetic saponite was used as solid sorbent. The uptake tests were performed in pure water at two pH values (3, 6), working with a metal concentration of 10 mM. The saponite showed high effective sorption capacity for all the metals analysed at both pH values after 24 h. The relaxometry data agree with those obtained from ICP technique. Furthermore, the re-generation of the clay was evaluated, together with the recovering of the metals trapped in the solid. The results obtained proved the effectiveness of the NMR relaxometry for the study of the uptake & recovery of paramagnetic metals from water, especially compared to traditional analytical techniques and considering the simplicity and non-destructiveness of the relaxometric analyses.

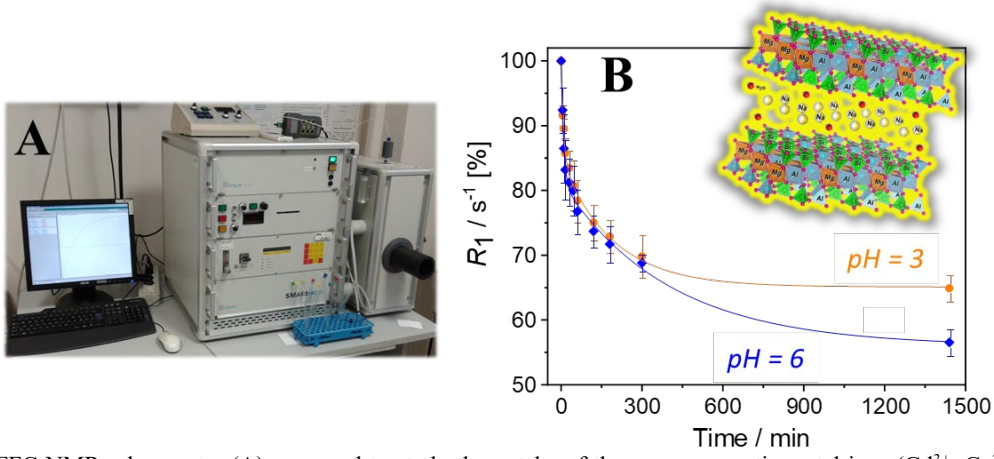

Figure 1. FFC-NMR relaxometer (A) was used to study the uptake of three paramagnetic metal ions (Gd^{3+}, Cu^{2+}, Co^{2+}) in water with a synthetic saponite clay, by analysing the evolution of the R_1 parameter over time at two pH values (B).

[1] A) R. Ronda, T. Jüstel and H. Nikol, *J. Alloys Compd.*, **1998**, *275-277*, 669-676; B) J. Malinowski, D. Zych, D. Jacewicz, B. Gawdzik and J. Drzeżdżon, *Int. J. Mol. Sci.*, **2020,** *21*, 5443-5468.
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[3] Y. Gossuin and Q. L .Vuoong, *Sep. Purif. Technol.*, **2018**, *202*, 138-143.

Template assisted sol-gel synthesis of Fe-doped TiO_2 with photocatalytic activity under visible light

Nicola Blangetti[a], Antonietta Mancuso[b], Olga Sacco[c], Vincenzo Vaiano[b], Barbara Bonelli[a], Serena Esposito[a], Francesca S. Freyria[a], Diana Sannino[b]

[a] *Department of Applied Science and Technology and INSTM, Unit of Torino Politecnico, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino Italy, barbara.bonelli@polito.it, serena_esposito@polito.it, francesca.freyria@polito.it, nicola.blangetti@polito.it ; [b] Department of Industrial Engineering, University of Salerno, via Giovanni Paolo II, 132, 84084 Fisciano, SA, Italy, anmancuso@unisa.it, vvaiano@unisa.it, dsannino@unisa.it; [c] Department of Chemistry and Biology "A. Zambelli", University of Salerno, via Giovanni Paolo II, 132, 84084 Fisciano, SA, Italy; osacco@unisa.it*

Fe-doped TiO_2 photocatalysts (with 1, 2.5 and 3.5 wt. % Fe nominal content) were prepared by a soft-template assisted sol-gel approach in the presence of the triblock copolymer Pluronic P123. An undoped TiO_2 photocatalyst was also prepared for comparison. The Fe doping procedure was made with the aim of improving the photocatalytic activity under visible light: photocatalytic degradation of the azo-dye Acid Orange 7 (AO7) was studied under visible light and in the presence of different scavengers. The photocatalysts were characterized by means of X-ray powder Diffraction (XRPD), Quantitative Phase Analysis as obtained by Rietveld refinement, Diffuse Reflectance (DR) UV−Vis spectroscopy, N_2 adsorption/desorption at −196 °C, electrophoretic mobility in water (ζ-potential), IR spectroscopy and X-rays photoelectron spectroscopy (XPS). Table 1 gathers the most relevant results of the physico-chemical characterization.

Sample	Crystallite size (nm)[a]	QPA results (wt.%) [b]	pH_{IEP}	SSA ($m^2 g^{-1}$)[c]	Total Pore Volume($cm^3 g^{-1}$)	Band gap energy (Eg, eV) [d,e,f]	Average value of Eg	Nominal Fe/Ti atomic ratio	XPS surface Fe/Ti atomic ratio
TiO_2	10.0 ± 0.6 (A)	100 (A)	2.36	150	0.28	3.28,[d] 3.35 ,[e] 3.32[f]	3.31	0	0
Fe(1.0)-TiO_2	9.4 ± 0.4 (A)	100 (A)	4,14	135	0.25	3.10,[d] 3.01[e] 3.08 [f]	3.06	0.014	0.034
Fe(2.5)-TiO_2	8.4 ± 0.6 (A)	100 (A)	4.58	130	0.25	2.88,[d] 2.74[e], 3.03 [f]	2.88	0.037	0.069
Fe(3.5)-TiO_2	7.1 ± 0.6 (A)	100 (A)	5.08	145	0.24	2.99,[d] 2.70[e], 3.02 [f]	2.90	0.052	0.128

Tabel 1 [a] As obtained by applying the Williamson-Hall method.[b] As obtained by Rietveld refinement.[c] As obtained by applying the BET method.[d] As obtained by linear extrapolation of the DR UV-Vis spectra absorption edge. [e] As obtained by applying the Tauc's plot method for indirect band gap semiconductor $(F(R)*h\upsilon)^{1/2}$. [f] As obtained by applying the method reported in ref [1]

All the samples were 100 % anatase phase, and t iron was present both in the bulk and at the surface of the Fe-doped TiO_2 samples. The samples surface area and porosity were mildly affected by the presence of Fe, as well as the NPs morphology. ζ-potential measurements showed that Fe affected the surface, likely due to the presence of Fe oxo/hydroxide clusters, as shown by UV-Vis spectroscopy. Accordingly, XPS analysis showed that a higher concentration of Fe species at the surface, likely due to the adopted synthesis procedure. Fe doping also affected the bulk, as shown by the band gap energy (Eg) decrease with increasing Fe content. Successive tests also allowed to determine the k_{dec} for decoloration and k_{min} for mineralization: in both cases the kinetic mathematical model applied for photocatalytic reactions is that of Langmuir-Hinshelwood which, at low initial concentration of pollutants, can be reduced to a pseudo first order kinetics. The fast discoloration rate of the AO7 solution and therefore the highest photocatalytic activity was found for the Fe(2.5) -TiO_2 sample. Similar trends were observed with the k_{min} values. According to the photocatalytic activity results under visible light, the optimal Fe loading content was equal to 2.5 wt. % (Tauc's plot determined Eg = 2.74 eV), whereas at higher Fe content the formation of defects likely lowers the photocatalytic activity.

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Physico-chemical characterization of high surface area TiO_2

Chiara Nannuzzi,[a] Jennifer M. Houghton,[b] Anders H. Pedersen, [b] Peter N. R. Vennestrøm [b] Ton V.W. Janssens, [b] Lorenzo Mino [a] Maria C. Paganini [a] Silvia Bordiga [a] and Gloria Berlier [a]

[a] Department of Chemistry, NIS and INSTM Centers, Università di Torino, via P. Giuria 7, 10125-Turin, Italy
b Umicore Denmark ApS, 2970 Hørsholm, Denmark.

Titanium dioxide is widely used for many applications such as photocatalysis, photovoltaics and as a support for active phases in many catalytic reactions. Apart from crystal structure (anatase *vs* rutile), morphology, particle size and surface structure are important parameters affecting TiO_2 performance in many applications.[1] One of the most desirable properties (particularly in catalysis) is a high surface area, which is around 60 m^2/g for the benchmark TiO_2 material, P25.
In this work, the attention is focused on a high surface area TiO_2 anatase material (HS-TiO_2, 390 m^2/g), to be used as support for active phases in catalytic processes. The synthesis of oxide-based catalysts often requires at least one calcination step. This implies that to obtain a highly dispersed active phase it is important to understand how the properties of the support are affected by thermal treatments.
To this aim, structure, morphology, particle size and textural properties of HS-TiO_2 have been studied as a function of thermal treatment conditions (temperature, length, humidity, etc.). Figure 1 reports representative TEM images of HS-TiO_2 calcined at 350 °C, compared to a 'standard' anatase samples (STD-TiO_2) with surface area around 80 m^2/g. The particle growth and agglomeration as a function of the calcination temperature results in changes in surface area and porosity.

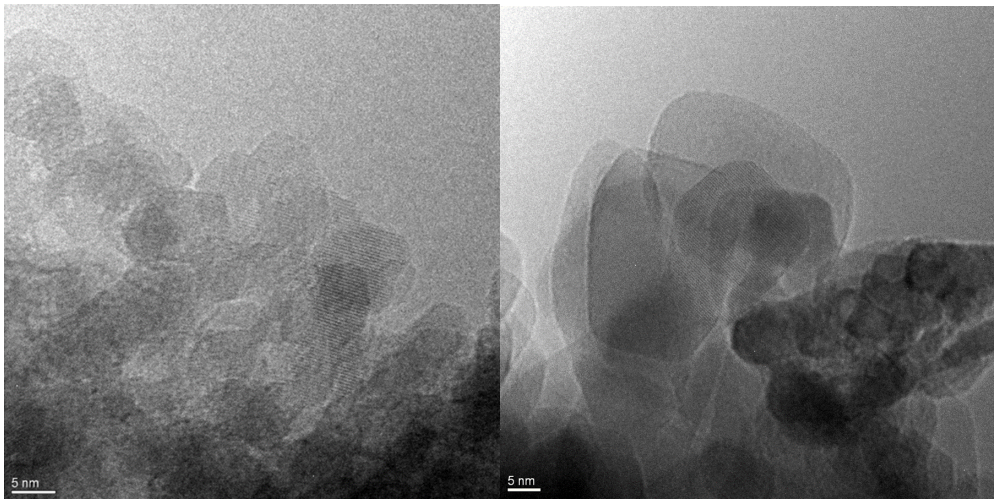

Figure 1 HR-TEM images of HS-TiO_2 material calcined at 350°C for 1h (left) and STD-TiO_2 (right).

In situ infrared spectroscopy was used to analyze the exposed surfaces of the two materials, by analysis of the OH stretching region and by use of probe molecules (CO and NH_3) after thermal treatments in flow or in vacuum, following well-established metholodogies.[2,3] The two samples qualitatively show a similar surface structure (in terms of OH, Ti^{4+} surface sites and defects), with differences in the amount of defects and OH groups, which are rationalized by thermogravimetric analysis.

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Nano-TiO_2 based material for environmental and antibacterial application

Massimo Dell'Edera [a,b], Ilaria De Pasquale [b], Chiara Lo Porto [b], Elisabetta Roberto [a], Angela Agostiano [a,b], M. Lucia Curri [a,b] and Roberto Comparelli [b]

[a]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Via Orabona 4, 70126 Bari, Italy; [b]CNR-IPCF, Istituto per i Processi Chimico-Fisici, S.S. Bari, c/o Dip. Chimica Via Orabona 4, 70126 Bari, Italy

In recent years, one of the most important concern for the scientific community and for the human policy is the protection of people health trough a smart and sustainable use of environmental resources [1]. In this framework, has become more interest for the scientific community the use of TiO_2 based nano-material. Indeed, TiO_2 nanoparticles (NPs) with their excellent photocatalytic performance are among the most investigated semiconductor materials for environmental clean-up applications[2] as photocatalytic degradation of organic pollutants from water, and for the disinfection/inactivation of harmful pathogens including bacteria, viruses, and fungi.[3] However, aside from the superior advantage of TiO_2 nanostructured materials, some drawbacks have been identified, i.e., high recombination rate of the photogenerated species and limited solar light sensitivity, therefore various modifications have been developed to enhance the photocatalytic efficiency. In this work nano-TiO_2 based NPs were synthesized using a co-precipitation method.[4] Therefore, TiO_2-based nanomaterials such as pristine TiO_2 ,TiO_2/Au nanorods and TiO_2/Ag were characterized by X-ray diffraction analysis, TEM analysis, SEM analysis and diffuse reflectance spectroscopy. The degradation properties of organic pollutants in the aqueous matrix of nanomaterials were initially studied using a model pollutant, i.e. a methylene blue dye, and then by studying the degradation of trimethoprim. Finally, antibacterial properties of TiO_2 and TiO_2/Ag were studied using *E.coli* like target microorganisms.

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Combining Morphology, Surface Fluorination and Au Nanoparticles Deposition on TiO_2: Effects on Rhodamine B Photodegradation

Marco Montalbano,[a] Maria Vittoria Dozzi,[a] Gianluigi Marra,[b] Elena Selli[a]

[a] Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy. [b] Renewable Energy and Environmental R&D, Istituto Eni Donegani, Via Fauser 4, I-28100 Novara, Italy

The performance of titanium dioxide, the most widely studied photocatalyst, is known to deeply depend on its structural, electronic, and surface properties. Among the many strategies employed to improve its photoefficiency, a lot of attention has been devoted to tuning the anatase crystals towards a platelet-like morphology, due to the higher reactivity of the {001} facets compared to the {101} ones. An improved charge carrier separation efficiency may be also offered by the preferential migration of electrons and holes towards the {101} and {001} facets, respectively [1]. The photoactivity of TiO_2 may also be improved through *in situ* surface fluorination, with effects depending on the surface area and phase composition of TiO_2 [2], and by metal nanoparticles (NPs) deposition, able to suppress electron-hole recombination. In this scenario, the present work aims at studying if and how the effects on photoactivity of TiO_2 surface fluorination, eventually also coupled with surface Au NPs deposition, depend on the specific TiO_2 morphology.

Home-made anatase nanocrystals, characterized by a pseudo-spherical or nanosheet morphology, were thus synthesized using a typical hydrothermal route (180 °C for 24 h), modified with 0.5 wt% metal Au through a modified version of Haruta's deposition-precipitation (DP) method or by photodeposition (P) [3-4], and fully physico-chemically characterized. The photoactivity of these powders was tested in the photocatalytic oxidation of Rhodamine B (RhB) at pH 3.7 under UV-Vis irradiation, both in the presence and in the absence of *in situ* added fluoride anions.

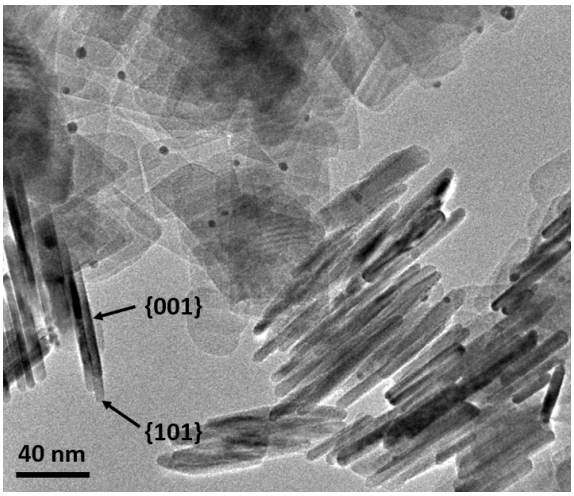

Figure 1: TEM image of TiO_2 nanosheets modified by Au NPs photodeposition.

A clear synergistic effect between morphology control and surface fluorination was observed in the case of bare, metal-free TiO_2 powders, in which a remarkable activity improvement towards RhB oxidation was observed upon surface fluorination of the nanosheet-shaped material compared to pseudo-spherically shaped crystals, possibly due to an intrinsic capability of F-{001} facets in boosting $^{\bullet}OH$ radical mediated oxidation paths. Under *in situ* fluorinated conditions, also the interaction between deposited Au metal NPs and the metal oxide support is influenced by the morphology of anatase nanocrystals. In fact, whereas in the case of pseudo-spherically shaped materials the same activity improvement was obtained with materials prepared by Au NPs deposition by the DP or the P method, in the case of TiO_2 nanosheets a beneficial effect in boosting photoactivity was obtained only in materials prepared by photodeposition, possibly due to an intrinsic ability of this method to selectively deposit metal NPs onto {101} facets.

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Chemical-physical methods to investigate properties of vegetable oils and fats

M. F. Colella[a,b], P. Caputo[b], N. Marino[c], G. De Luca[a], C. Oliviero Rossi[b]

[a]LXNMR_S.C.An. Laboratory; [b]Applied Industrial Physical Chemistry Group, [c]MAT-in LAB; Department of Chemistry and Chemical Technology (CTC), University of Calabria, Arcavacata di Rende (CS) – Italy

In food industry research, particularly in recent years, ease of transport, processing and storage of products has to reconcile with the request of good foods having a beneficial impact on human health and protecting body from diseases. For example, various families of long-chain phyto Fatty Acids (FAs), according to the most recent recommendations[1], should not exceed 30% of the daily calorie intake in a balanced and salutary diet and some vegetable oils and fats, with a specific lipidic composition, seems to be the best sources of healthy FAs.
The focus of this work is to examine the chemical and physical behaviour of a natural and modified vegetable fats obtained for the first time, to understand which factors could be responsible for its physical and chemical characteristics. For this purpose, the experimental investigation carried out, both at a macroscopic and at molecular level, includes: i) rheological testing to explore mechanical properties; ii) DSC tests to examine thermal features; iii) NMR (1D and 2D) Spectroscopy for a molecular characterization[2]; iv) X-Ray diffraction to observe, still preliminarily, fats crystalline form and an eventual polymorphism[3].
The accordance between experimental results from these different techniques confirms how a specific chemical and physical behavior and their physical state are largely determined not only by the type and quantity of Fatty Acids, but also by their stereospecific positioning in TriAcylGlycerols (TAGs). This is fundamental because the modification process allows manipulating the distribution of Fatty Acids but not their nature, so the initial percentage of each FAs in mixture remains the same. Moreover, the stereospecific position, also with chain length of fatty acids, determine the metabolic fate of dietary fat during digestion and absorption, so an inversion of this distribution on glycerol backbone could favor also a specific and better absorption in the human body[4].

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When the Solute is Completely Slaved to the Solvent:Jump Reorientation of Formamide in Water

M. Paolantoni [a], S. Perticaroli [b], L. Comez [c,d], P. Sassi [a], D. Fioretto [d], A. Morresi [a]

[a] Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Perugia, Italy;[b] Department of Chemistry, University of Tennessee, USA;[c] CNR-IOM, c/o Dipartimento di Fisica e Geologia, Università di Perugia, Perugia, Italy;[d] Dipartimento di Fisica e Geologia, Università di Perugia, Perugia, Italy;

Water has unusual properties that crucially depend on the H-bonding structure and dynamics. The molecular reorientation of water has been successfully described considering a jump mechanism, leading to a consistent picture of the H-bond reorganization at picosecond (ps) time scales [1,2]. In this context, the study of neat formamide (FA) and its aqueous solutions may provide further fundamental insights on the intermolecular structure and dynamics in other associated systems, whose properties stronghly depend on H-bonding features [3].
Here, the orientational dynamics of FA in aqueous solutions is investigated by means of high-resolution depolarized light scattering experiments, which probe the relaxation of the total anisotropic polarizability of the system. The dynamical susceptibility is measured over a broad frequency range (0.01-1000 cm^{-1}) through the combined use of dispersive and interferometric instruments. This approach, referred to as *Extended Depolarized Light Scattering* (EDLS) [4], was proven suitable for the study of the molecular mobility in aqueous solutions of biorelevant systems at time scales ranging from fractions to hundreds of picoseconds [5,6].
The results obtained for neat FA and FA-water solutions at different concentrations and temperatures will be presented. The relaxation dynamics (tens of ps) and the low-frequency intermolecular Raman modes (fractions of ps) are analyzed and interpreted in connection with the organization of the H-bonding network formed by the two species and by their dynamical coupling. One of the main achievements of this study is the experimental evidence that, in diluted conditions, FA reorientation is completely determined by that of water [7].

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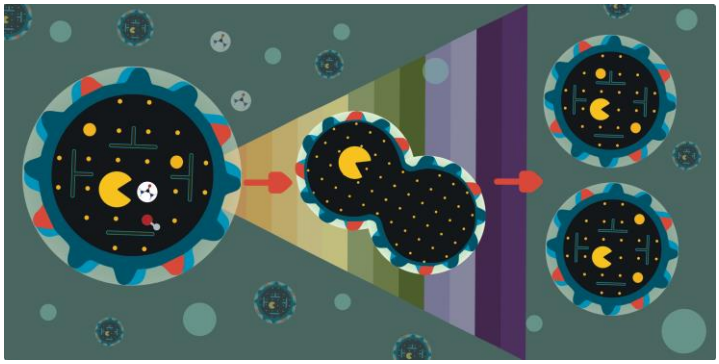
Shape Transformation of Artificial Vesicles Induced by an Interplay between Osmosis and pH Change

Gabor Hollo,[a] Ylenia Miele,[b] Nadia Marchettini,[c] Istvan Lagzi[a] and Federico Rossi[c]

[a] *MTA-BME Condensed Matter Physics Research Group, Budapest University of Technology and Economics 1111, Budafoki ut 8, Budapest, Hungary*
[b] *Department of Chemistry and Biology ''A. Zambelli''University of Salerno, Via Giovanni Paolo II 132, 84084 - Fisciano (SA), Italy*
[c] *Department of Earth, Environmental and Physical Sciences - DEEP Sciences, University of Siena, Pian dei Mantellini 44, 53100 - Siena, Italy.*



Shape transformation and self-division of phospholipid/fatty acid giant hybrid vesicles can be induced by an internal chemical stimulus (pH change) when coupled with an osmotic shock [1,2]. In particular, an autocatalytic enzymatic reaction set (urea-urease system), confined in the lumen of 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC)/oleic acid (HOA) vesicles, can force the budding or the division of the hosting vesicle, when properly fed by a trans-membrane substrate (urea) infusion. Here we discuss the mechanism responsible of the membrane deformation in terms of physical (bending modulus) and chemical (acid-base equilibria) basis and in the light of the area-difference-elasticity (ADE) theory [3]. Such a mechanism would help the development of stimuli-responsive vesicles for drug delivery systems.

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Shelf-life prediction of paracetamol formulations by non-isothermal thermogravimetry

Martina Maria Calvino [a], Lorenzo Lisuzzo [a], Giuseppe Cavallaro [a], Giuseppe Lazzara [a], Stefana Milioto [a]

[a] Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze, pad. 17, 90128, Palermo, Italy;

Pharmaceutical formulations are composed of active molecules and several excipients that affect the stability and the release properties of the final products. Therefore, the shelf-life represents a key parameter of the drug quality and an accurate estimation is challenging in pharmaceutical technologies. It can be conducted by accelerated degradation conditions. As a matter of facts, non-isothermal thermogravimetric studies have been performed on paracetamol formulations as accelerated tools to predict their shelf-lives under variable storage conditions. Particularly, the study was conducted on paracetamol tablets produced by various industries worldwide allowing to estimate their pharmaceutical quality by considering the specific drug stability.
The proposed protocol consists on the kinetic analysis of thermogravimetric data collected at five variable heating rates by the combination of two isoconversional procedures (Friedman and Kissinger-Akahira-Sunose (KAS) methods) and "Master plot" analysis. Therefore, the kinetics of the paracetamol degradation is totally examined in terms of activation energy, pre-exponential factor and reaction mechanism of the drug decomposition.
These results lead to simulate the decay time functions of paracetamol amount for the several pharmaceutical formulations. Interestingly, shelf-lives of the paracetamol tablets at different temperatures were obtained because these simulations can be easily adapted to variable isothermal conditions. The kinetic characteristics of the paracetamol degradation as well as the corresponding shelf-life values evidenced that the expiration date, namely the stability, of the pharmaceutical products are significantly related to the peculiar composition of the excipients in the formulations. In conclusion, this work demonstrates that non-isothermal thermogravimetric analysis can be used as efficient and sensitive tool for the prediction of the shelf-lives of paracetamol formulations.

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Stability of protein-polymer conjugates in solution

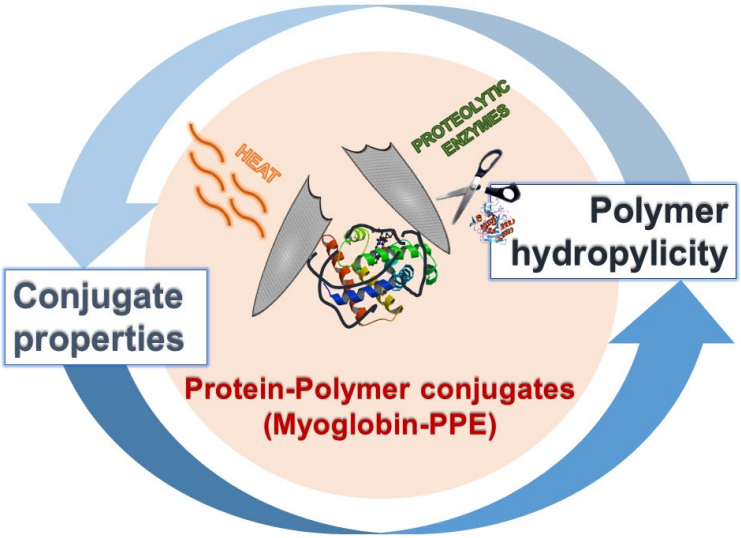
Chiara Pelosi [a], Frederik Wurm [b], Celia Duce [a], Maria Rosaria Tinè [a].

[a]: Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi, Pisa 56124, Italy. [b]: Sustainable Polymer Chemistry Group, MESA+ Institute for Nanotechnology, Faculty of Science and Technology, Universiteit Twente, PO Box 217, 7500 AE Enschede, The Netherlands.

Protein-polymer conjugates are a new class of biohybrids with high potential in the biomedical field [1]. Beyond the synthesis, a biophysical evaluation of the conjugates is necessary to orientate the design of future candidates.

We prepared a novel class of PPE-ylated conjugates [2] (made by the model protein myoglobin and the polymers polyphosphoesters), focusing our attention on the polymer role in the physical and thermal stability of the protein in solution. We performed measurements by Circular Dichroism (CD) spectroscopy, UV-Vis spectroscopy, Nano-Differential Scanning Calorimetry and Fluorimetry, observing the stability of the samples during a temperature scan, in presence of denaturants or proteolytic enzymes.

Overall, with all the techniques, we observed a decreasing stability with increasing the hydrophobicity of the attached polymers [3]. In particular, calorimetry showed that in the conjugates the protein unfolding enthalpy and temperature decrease, but the more hydrophilic polymers enhance the protein thermal reversibility, reducing thermally-induced aggregation phenomena. This behaviour was confirmed by CD measurements, used also to assess the protein denaturation at different pHs or urea concentrations. UV-Vis absorbance was employed to observe the degradation of the samples in presence of proteolytic enzymes, which confirms the protective action of hydrophilic polymers, while the more hydrophobic polymers enhance the protein degradation rate.



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Kinetics and mechanism of 4-hydroxybenzoic acid degradation by persulfate/MnO_2 oxidation

Stefano Salvestrini[a,b]

[a] *Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, University of Campania "Luigi Vanvitelli", via Vivaldi 43, 81100 Caserta, Italy;* [b] *Environmental Technologies, University Spin Off of University of Campania "Luigi Vanvitelli", Via Vivaldi, 43, 81100 Caserta, Italy*

4-hydroxybenzoic acid (HBA) is a representative compound of phenolic water pollutants. It is harmful for microorganisms and recalcitrant to conventional biological water treatment processes [1], thereby requiring alternative methods for its removal.
Advanced oxidation processes (AOPs) are promising technologies that use reactive species, such as hydroxyl (•OH) and sulfate ($SO_4^{\bullet-}$) radicals, for the removal of persistent organic compounds from water. $SO_4^{\bullet-}$ radicals are particularly effective, mostly because of their higher redox potential and relatively long life time. They can be generated from the activation of persulfate (PS) by means of heterogeneous transition metal catalysts such as Mn-oxides. Mn-oxides have drawn the attention of the scientific community due to their low cost, natural abundance and environmental friendly characteristics [2].
In this work, the kinetics of degradation of HBA by PS and MnO_2 was studied. The reaction mixtures were analyzed by HPLC under different experimental conditions, by varying pH, temperature, PS concentration and MnO_2 dosage. In the absence of MnO_2, the reaction was found to be of zero-order and first-order with respect to HBA and PS, respectively. The co-presence of PS and MnO_2 led to a very fast and efficient removal of HBA from water, owing to a synergic effect between the two catalysts (Fig.1). HPLC analysis of the samples revealed that 1,4-Benzoquinone (BQ) was the only oxidation product detected in appreciable amount. Remarkably, BQ similarly to HBA, was fully degraded during the reaction, thus clearly suggesting that the oxidation process likely led to the complete mineralization of 4HBA.
A kinetic model for describing the rate of HBA degradation induced by the PS/MnO_2 system was proposed and successfully applied to the experimental data.

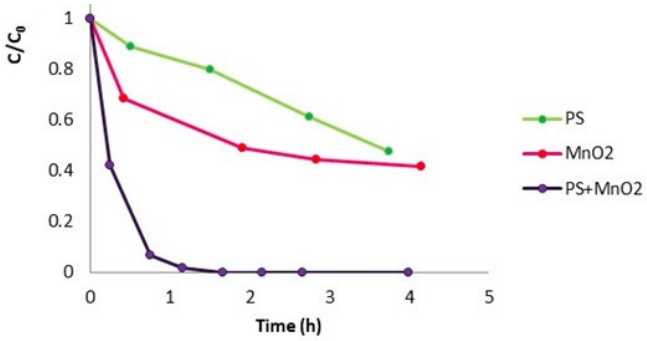

Fig.1. Degradation kinetics of HBA in the presence of PS, MnO_2 and both catalysts. Initial HBA concentration (C_0) = 0.2 mM; PS concentration = 16.8 mM; MnO_2 dosage = 2.4 g L^{-1}; temperature = 45 °C.

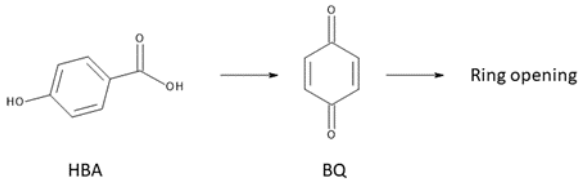

Fig.2. Reaction pathway for the oxidation of 4-hydroxybenzoic acid

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Unraveling the solvation properties of Lanthanide (3+) ions: from molecular solvents to Ionic Liquid based systems

Valentina Migliorati, Andrea Lapi, Matteo Busato, Paola D'Angelo

[a] *Dipartimento di Chimica, Università di Roma "La Sapienza", P.le A.Moro 5, 00185 Roma.*

Solvation is a complex phenomenon that lies at the basis of several chemical processes in solution and the capability of a given solvent to dissolve a compound depends on the nature of the solute and solvent. The dissolution of Lanthanide(III) (Ln^{3+}) ions in solvents with different polarity is widely employed for separation of these species in nuclear power technology and industrial processes. Even if conventional organic solvents have been the main choice in the past to extract Ln^{3+} ions from the aqueous phase, the possibility of employing ionic liquids (ILs) is being explored due to their excellent properties such as low vapor pressure, low combustibility, excellent thermal stability and favorable solvating properties for a range of polar and non-polar compounds. Moreover, one of the key principles of green chemistry is to use safer solvents and, in this respect, ILs are ideal alternatives since they are environmentally friendly. Therefore, an accurate atomistic description of the Ln^{3+} ion solvation structures in molecular solvents and IL media is an important piece of information both for basic research and to improve the efficiency of extraction procedures.

Despite their importance, the Ln^{3+} solvation properties are far from being completely understood. This is due to the fact that the investigation of the structures formed in liquid systems is in general a very difficult task. From an experimental point of view, X-ray absorption spectroscopy (XAS) is ideally suited to shed light on the local coordination geometries of an ion in solution but carrying out a reliable analysis of the XAS experimental data is not a trivial task when this technique is applied to the study of disordered systems. In the last years, it has been shown that very accurate structural information on liquid systems can be obtained by combining the XAS technique with Molecular Dynamics (MD) simulations.

Here, we will show how this powerful combined approach allowed us to unravel the Ln^{3+} coordination geometries in different liquid media. In particular, by combining XAS and MD we first developed new Lennard-Jones potentials involving Ln^{3+} ions for the whole Lanthanide series in water to be used in MD simulations of Lanthanide containing systems. These MD potentials have then been adopted to investigate the solvation properties of Ln^{3+} ions in more complex media, such as diluted solution of Ln^{3+} nitrates in the protic ionic liquid ethylammonium nitrate, acetonitrile solutions of Ln^{3+} bis(trifluoromethylsulfonil)imide ($Ln(Tf_2N)_3$) salts or solutions of $La(Tf_2N)_3$ in IL/acetonitrile mixtures. A general picture that can be drawn from our results is that Ln^{3+} coordination is mainly driven by electrostatic forces and, very interestingly, the solvation complexes formed by the Ln^{3+} ions show a great adaptability which allows the systems to reach the ideal compromise among all of the different forces into play (see Figure 1). Our results can also explain several characteristic behaviors of Ln^{3+}-based systems, such as the high catalytic activity of $Ln(Tf_2N)_3$ based complexes and the optimal properties of acetonitrile as solvent for catalytic reactions with Lanthanides.

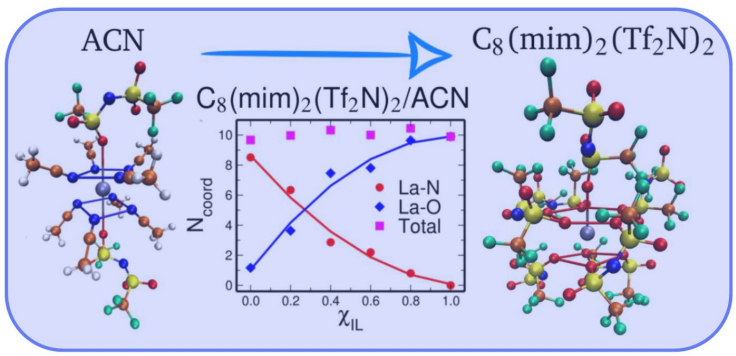


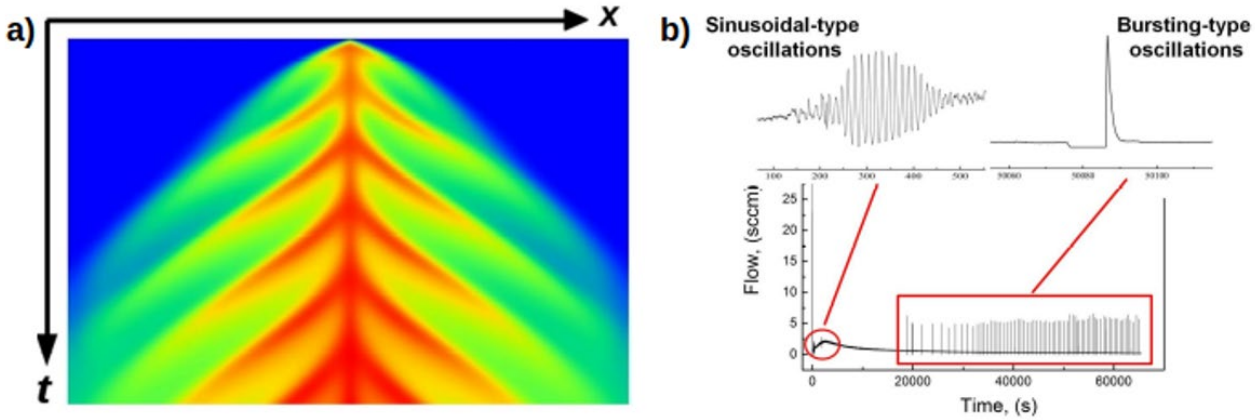
Figure 1. Evolution of the La^{3+} solvation shell from the pure acetonitrile (left) to the pure IL solvent (right).

Between dissipative structure and applications: chemical oscillations

M.A. Budroni [a], L. Rongy [b], G. Mulas [a], S. Garroni [a], M. Rustici [a]

[a]Department of Chemistry and Pharmacy, University of Sassari; [b]Nonlinear Physical Chemistry Unit, Faculté des Sciences, Université libre de Bruxelles (ULB)

Chemical reactions provide a fundamental means not only for the synthesis of new products but also for internal spatio-temporal self-organization [1]. Oscillatory dynamics and waves in inorganic chemical systems represent among the most fascinating examples of this chemically-driven order. For years at the center of an intense theoretical debate, these phenomena still pose open challenges at the heart of several problems as diverse as the imitation of neural activity [2], the development of brain-like chemical machines [3] and the design of a new generation of smart materials [4].
Here we discuss two examples pertaining both fundamental and applied aspects.
First, so far the understanding of chemical oscillations has involved the pivotal role of nonlinear chemistry. Is it possible to design autonomous oscillations with more ordinary chemical kinetics?
We show this possibility with simple and general bi-molecular processes which can yield spontaneous pulsatory behaviours, in the absence of any nonlinear or external chemical feedback, thanks to an active interplay between the chemical reaction and chemically-driven hydrodynamics [5].



a) Typical spatio-temporal evolution of chemohydrodynamic oscillations. b) Possible oscillatory regimes in the delivery of H_2 from the $NaBH_4$ hydrolysis.

After giving an overview of possible practical implications of the oscillatory scenarios mentioned above, we briefly illustrate a further concrete example where mastering nonlinear mechanisms allows to control unfavorable fluctuations occurring in the generation and delivery of molecular hydrogen from the hydrolysis of borohydride salts [6], which represents a promising process in the context of alternative fuels.

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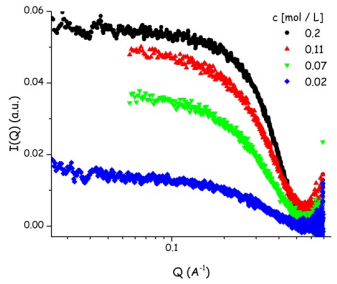
Nature of solvation of cyclodextrins in (protic) ionic liquids and deep eutectic solvents

Olga Russina[a], Fabrizio Lo Celso[b] and Alessandro Triolo[c]

[a] Department of Chemistry, University of Rome Sapienza, Rome, Italy[b] Department of Physics and Chemistry, University of Palermo, Palermo, Italy [c] Laboratorio Liquidi Ionici, Istituto Struttura della Materia, Consiglio Nazionale delle Ricerche, (ISM-CNR) Rome, Italy

*e-mail: olga.russina@uniroma1.it

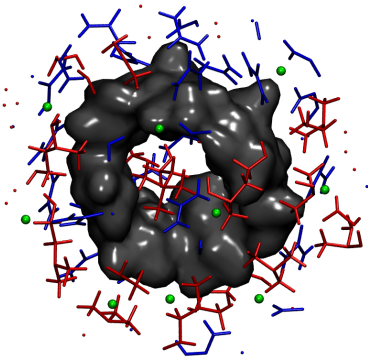
Cyclodextrins are doughnut-shaped macrocyclic molecules, whose geometry and chemical nature play a big role in accommodating several compounds of applicative interest in fields as wide as food and aromas technology, synthesis, catalysis. Very often their range of applications is severely limited by the poor solubility in water. Accordingly the exploitation of green, or at least environmentally compatible, solvent media that succeed in efficiently dissolving CDs could pave the way to substantial change in paradigm in CD exploitation.



SAXS patterns from mixtures of βCD in Ethylammonium Nitrate,

In this scenario we recently undertook a systematic exploration of microscopic organization of different CDs dissolved in ionic liquids (ILs) and deep eutectic solvents (DES). The latter are attracting great attention as environmentally responsible media due to appealing properties including negligible vapor pressure, high thermal stability and enhanced compatibility with a variety of different compounds. Furthermore DES sport very interesting features including their very cheap cost as well as their biocompatibility (some of them might even be edible (or, better, drinkable)).

A few reports appeared in the recent literature illustrating the high solubility of CDs in several ILs and DESs. This opens the way to several applications, but calls for detailed microscopic studies to explore the nature of CD dissolution in these media, both in order to rationalize and potentially further extend CD solubility. Experimentally X-ray Scattering techniques are ideal to probe the state of dissolved CDs. We explored several binary systems by SAXS aiming at understanding potential CDs aggregation that might limit performances and observed that in several cases CDs remain un-aggregated in these media even at high concentrations (e.g. as high as 150 mg/mL of βCD in Reline, a typical DES (for comparison, solubility of βCD in water is 18 mg/mL)).



MD-derived snapshot of βCD

To further explore these issues we conducted Molecular Dynamics simulations supported by X-ray scattering to access microscopic details on these systems.

Specific ions effects in green oleate-based formulations: how salts can influence the structure and rheology of viscoelastic systems

Duccio Tatini[a], *Barry W. Ninham*[b] *and Pierandrea Lo Nostro*[a]

[a] *Dept. of Chemistry and CSGI, University of Florence, 50019 Sesto Fiorentino (Firenze), Italy*[b] *Dept. Applied Mathematics, Australian National. University, Canberra ACT 0200, Australia*

Viscoelastic surfactant (VES) systems are based on low-molecular weight surfactants that can form "wormlike" micelles in solution. At moderate/high concentrations these structures produce a tight entangled network, giving rise to a viscoelastic behavior that recalls that of flexible polymer solutions and of bicontinuous three-component ionic microemulsions [1]. The addition of specific electrolytes and cosolutes brings about remarkable changes in the physicochemical and structural properties of these systems, as evidenced by our previous studies [2-3].
In this work we investigate the combination of moderately concentrated dispersions (0.43 M) of sodium and potassium oleate (NaOL and KOL), two green and safe anionic surfactants, with different salt solutions (0.27 and 0.54 M) to check the effects imparted by different ions on the phase behavior, the thermal and the rheological properties of these VES formulations. In this concentration range specific ion effects clearly emerge, and the electrostatic theory cannot provide an adequate explanation to the structural modifications occurring in the micellar network. The rheological behaviour and the thermal properties were investigated through viscosity measurements, frequency sweep tests and differential scanning calorimetry (DSC), respectively. The results show that the specific choice of cation-anion pairs has dramatic consequences on the stability and phase behavior of the formulations, revealing the overall relevance of non-electrostatic (e.g. hydration) interactions. The presence of the salt induces a remarkable change in the wormlike entangled structure of the pristine oleate-water system. This leads to a significant increase in the formulation viscosity and a variation of the dynamical rheological properties, depending on the nature and concentration of the salt.

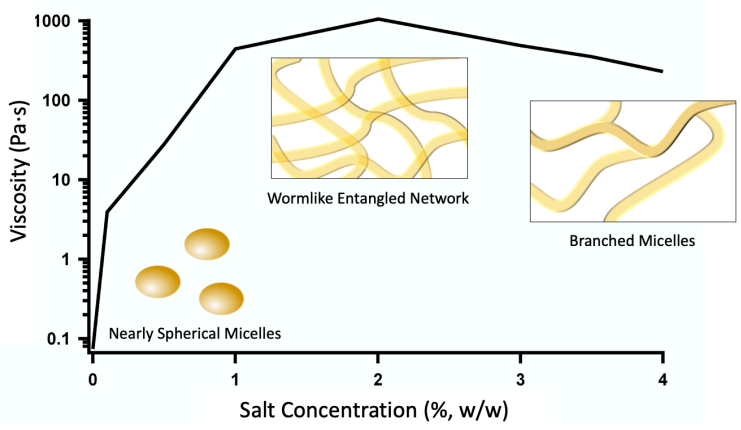


Figure 1. Synopsis of the rheological behavior and structural features of micellar aggregates formed by NaOL and KOL at different salt concentrations.

[1] C. Dreiss, *Soft Matter*, **2007**, *3*, 956.
[2] D. Tatini, M. Raudino, M. Ambrosi, E. Carretti, I. Davidovich, Y. Talmon, B.W. Ninham, P. Lo Nostro, *J. Colloid Interface Sci.* **2021**, *590*, 238.
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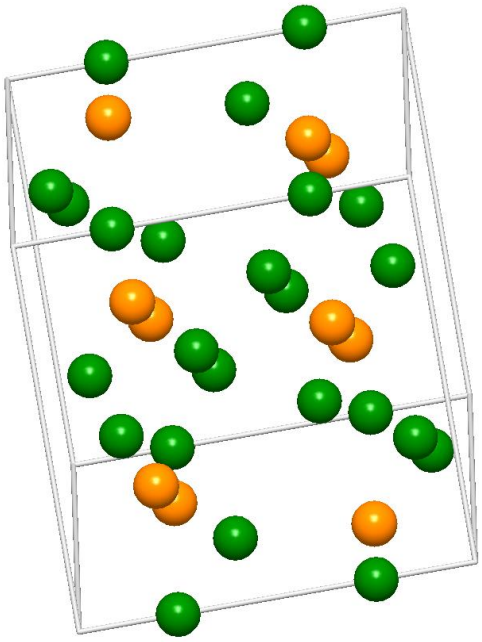
Structures and phase equilibria in the ternary Cu-As-Sb system (a preliminary investigation)

M. Mödlinger [a,], M. Pani [a], D. Macciò [a] , A. Ciccioli [b], P. Manfrinetti [a,c], M. Ferretti [a]*

*[a] Department of Chemistry, University of Genova, Genova, Italy; [b] Department of Chemistry, University of Rome I, Rome, Italy; [c] Institute SPIN, CNR, Genova, Italy; *e-mail: marianne.moedlinger@edu.unige.it*

An experimental investigation on the phase equilibria in the Cu-rich side of the ternary Cu-As-Sb system (65 – 100 at.% Cu), and on the crystal structure of the intermediate phases and intermetallic compounds formed, has been undertaken.



Cu3As (*hP24*, P-3c) [5]

A better understanding of this system will be strongly beneficial to the copper mining industry, especially when mining fahlores, other than for archaeological research. As and Sb improve hardness and oxidation resistance to the Cu, while significantly reduce the electrical conductivity.

While from the literature the respective single binary systems (Cu–As, Cu–Sb, As–Sb) appear relatively well studied [1-5], no data, neither on the ternary phase diagram nor on the crystallography of the ternary phases, have been reported so far. Moreover, and despite the number of articles published on these binary systems, an evident lack of information on structural refinements and of understanding of their crystallochemistry of even the binary compounds remains.

Techniques of X-ray diffraction (XRD) on single crystal and powders, optical and electron microscopy (LOM, SEM), analytical microprobe (EDX), differential thermal analyses (DTA) and micro-hardness measurements (Vickers), are used. The preliminary results obtained by this investigation will be presented.

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Cu^+ bi-pyridine based homoleptic complexes as catalysts for partial oxidation reactions: a Raman study

Alessandro Damin,[a] Barbara Centrella,[a] Gabriele Deplano,[a] Matteo Bonomo,[a] Matteo Signorile,[a] Claudia Barolo,[a] Silvia Bordiga[a]

[a] Dipartimento di Chimica, NIS and INSTM, Università di Torino, Via P. Giuria 7, 10143 Torino, Italia

Direct conversion of methane by oxygen into methanol (a partial oxidation reaction through C-H activation) and, more in general, selective oxidation of abundant C-H-containing molecules into valuable products, constitutes nowadays a highly desired goal, mainly justified by the increasing availability of natural gas and bio-masses. Taking inspiration by what is supposed to be the Cu based active site in p-MMO enzyme [1,2], a possible direction of work is considering metallorganic complexes based on 2,2'-bipyrdine (bpy) ligands complexing Cu species. One of these (*i.e.* 6,6'-dimethyl-2,2'-bipyridine, dmbpy) has already demonstrated to be useful in preparing tetrahedral $[Cu(dmbpy)_2]^+(PF_6)^-$ complex (see Figure 1, hereafter CuBP-M) as efficient redox mediator in dye sensitized solar cells [3]. In this case, the steric hindrance (due to substituent methyl groups) is supposed to destabilize the square planar coordination typical for Cu^{2+} ions, so increasing the possibility to continuously cycle between Cu^+ and Cu^{2+} species: it is worth noticing here, that the observed reversibility between the two Cu oxidation states could be exploited in obtaining an active catalyst in partial oxidation reactions: this, for instance, after the transformation of Cu^+ to a $[CuO_{active}]^+$ species by a suitable O containing agent. The understanding of the structure of Cu-complexes requires the adoption of techniques capable of disclosing the local structure of the system around the metal center depending on its oxidation state. This ambitious target requires the combined use of a multi-technique approach, possibly conducted simultaneously: this was the case pursued in this study that saw the adoption of Raman and UV-Vis Spectroscopy, Cyclovoltammetry, and DFT based calculations. CuBP-M was studied in dichloromethane (DCM) solutions, following its modification upon the interaction with tert-butyl-hydroperoxide (tBu-OOH), the chosen oxidant agent. To get insights on the effect of methyl groups in 6-6' position, the analogous $[Cu(bpy)_2]^+(PF_6)^-$ complex (CuBP-H) was investigated too. The simultaneous use of UV-Vis and Raman Spectroscopy, supported by Cyclovoltammetry and DFT based calculations, allowed to identify a) the change in the oxidation state of the copper ion, b) some peculiar modification in the local structure of the Cu species (*e.g.* through a different vibrational response of the ligands), possibly transformed in a generic $[CuO]^+$ species. In the case of CuBP-M complex, the relevance of the formed $[CuO]^+$ was confirmed by the further reactivity of such species with a model molecule (cyclohexene) that showed the restoration of the original Cu^+ confirming the interest of these complexes as model catalysts for partial oxidation reactions. ERC-SyG project CUBE (project nr. 856446) is acknowledged for financial support.

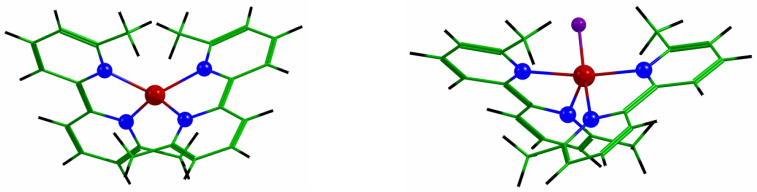

Figure 1: CuBP-M ($(PF_6)^-$ omitted for clarity) complex (on the left) and a tentative structure of the oxidized one (on the right) bearing a generic *O* species (purple sphere).

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[3] Y.Saygili, M. Söderberg, N. Pellet, F. Giordano, Y. Cao, A. B. Munoz-García, S. M. Zakeeruddin, N. Vlachopoulos, M. Pavone, G. Boschloo, L. Kavan, J. E. Moser, M. Gratzel, A. Hagfeldt, M. Freitag, *Journal of American Chemical Society* **2016**, 138, 15087.

Ultrasound-stimulated PVA microbubbles as removal tool for adhesive tapes from cellulose-based materials

Leonardo Severini [a], *Alessia D'Andrea* [a], *Fabio Domenici* [a], *Sultan B. Dabagov* [b, d, e], *Valeria Guglielmotti* [b, c], *Dariush Hampai* [b], *Laura Micheli* [a], *Ernesto Placidi* [f], *Mattia Titubante* [a], *Claudia Mazzuca* [a], *Gaio Paradossi* [a], *Antonio Palleschi* [a]

[a] *Department of Chemical Science and Technologies, University of Rome "Tor Vergata", Via Della Ricerca Scientifica 1, 00133 Rome, Italy;* [b] *INFN-LNF, XLab Frascati Via Enrico Fermi 54, 00044 Frascati (RM), Italy;* [c], *University Guglielmo Marconi, Via Plinio 44, 00193 Rome, Italy;* [d] *RAS P.N. Lebedev Physical Institute, Leninsky pr 53, 119991 Moscow, Russia;* [e] *National Research Nuclear University MEPhI, Kashirskoe Sh. 31, 115409 Moscow, Russia;* [f] *Department of Physics, Sapienza University of Rome, P.le Aldo Moro 2, 00185, Rome, Italy*

Preservation of paper manufacts plays a relevant role in the cultural heritage field, since a huge part of the mankind written knowledge from the last centuries was entrusted to paper. In this context, one of the primary and challenging issues is the removal of modern adhesives whose presence enhances paper degradation and worsens its optical features [1-2]. This work focuses on the development of a cleaning strategy based on ultrasound-stimulated PVA microbubbles (MBs) aimed at removing modern adhesive residues from modern paper (Fig.1). This idea is based on the finding that profilometry analysis indicates that surface depressions of several microns wide are present in the paper coated by adhesive, which are compatible with the MBs size. MBs can adhere well to the surface of the adhesive and perform near-field cavitation effects such as microstreaming flows and the progressive adhesive detachment. To assess our idea, we characterized the interaction of PVA microbubbles with paper and their cleaning efficacy by using several experimental techniques, like ATR–FTIR spectroscopy, fluorescent confocal microscopy, colorimetry and pH measurements. Moreover, HPLC proved the absence of residuals, while XRD and tensometry assess the integrity of the paper samples after the treatment. The final outcome is a treatment providing results comparable to those of classical treatments with solvents but faster (it takes only 2 min of application) with the advantage to avoid the use of substances potentially harmful for both restorers and artworks due to their chemical aspecificity [1-2]. Moreover this cleaning strategy proved to and versatile, thanks to the possibility of tuning the intensity and the duty cycle of the US delivery depending on the kind of sample and the substances to be removed. This is the first time (at the best of our knowledge) that ultrasound has been combined with microbubbles for the selective removal of a coating from a delicate substrate.

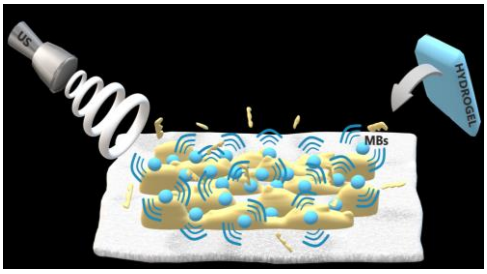

Figure 1. *Schematic representation of US-stimulated PVAMBs adhesive removal.*

[1] C. Pan, L. Industry, W. Tan, B. Kuang, Y. Fang, Y. Lin, X. Cai, *Wood Res.*, **2019**, 64, 759-772.
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Unusual corrosion of bronze helmets discovered in Mediterranean seabed

Francesco Armetta [a,], Maria Luisa Saladino [a], Antonella Scherillo [b], Eugenio Caponetti [c]*

[a] Dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche - STEBICEF, Università di Palermo, Viale delle Scienze Ed. 17, Palermo I-90128, Italy; [b] Science and technology Facility Council, ISIS Neutron and Muon Source, OX110QX (UK); [c] Labor Artis C.R. Diagnostica S.R.L., Via Celona, Palermo, Italy

A study of two type-Monterfortino helmets, exhibited in the Museo Archeologico Baglio Anselmi of Marsala (Trapani, Italy), is reported. Their general features are unusual respect to the more common helmets belonging to the same period and founded in underwater environments. For this reason, they were investigated by a multianalytical approach in order to provide an explanation of the degradation process occurred. A combined use of not-invasive and then micro-invasive analysis surface and bulk techniques (based on neutron [1] and X-Ray techniques) allowed us to obtain a deep profile composition.
It was found that the helmets were originally made in bronze and, the copper turned totally into sulphides, including shell-fish, during the process, and maintaining the original shape of the objects. In the complex structure of helmets matrix, crystals of different size and morphology were observed. The almost complete transformation of the original alloy into copper sulphides represents an unusual case of seawater degradation. Due to the presence of nantokite (CuCl) in the internal samples collected in both helmets, it is reasonable to assume that the corrosion started with the formation of copper (I) chlorine [2].
The identification in the inner part of digenite ($Cu_{1.9}S$) implies the corrosion process continued with the formation of the sulphide, a process justified by anaerobic and sulphides rich conditions that are usually founded in polluted areas, but that in the present case can be attributed to the sand covering.
The pervasive presence of covellite (CuS) implies that, after some time, the helmet was subjected to a higher oxidizing potential which promotes the conversion of digenite. This process can be justified supposing that the helmet was uncovered by the sand and spent some time on the seabed surface. In the case of helmet 2 the presence of covellite as the only sulphide indicates that digenite was totally converted and thus, that it spent more time on the seabed surface uncovered by the sand.
The explanation of helmet corrosion processes makes possible to hypothesize the reasons why the helmets maintained their original shape. The initial formation of copper (I) species (nantokite and digenite), through an epitactic transformation, maintained the helmets shape. The subsequent formation of copper (II) species in the solid-state topotactic transformation caused a slight alteration of the crystal lattice avoiding damage of the corrosion layer.

[1] G. Festa, T. Minniti, L. Arcidiacono, M. Borla, D Di Martino, F. Facchetti, E. Ferraris, V. Turina, W Kockelmann, J. Kelleher, R. Senesi, C. Greco, C. Andreani, Angewandte 130, **2018,** 7375-7379.
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F.A. thanks the MIUR for the Project PON Ricerca e Innovazione 2014-2020 – Avviso DD 407/2018 "AIM Attrazione e Mobilità Internazionale" (AIM1808223).

pHEMA/PAA and pHEMA/PVP semi-IPNs: physico-chemical characterization and use for bronze cleaning

*Teresa Guaragnone[a], Marta Rossi[a], **David Chelazzi**[a], Rosangela Mastrangelo[a], Mirko Severi[b], Emiliano Fratini[a], Piero Baglioni[a]*

[a] Department of Chemistry and CSGI, University of Florence; [b] Department of Chemistry, University of Florence

Bronze artifacts constitute an invaluable part of our Cultural Heritage, yet they are endangered by corrosion processes, such as the infamous "bronze disease" [1]. Current restoration practice lacks effective methodologies for the safe and controlled removal of corrosion products. Targeting this issue, we developed networks of poly(2-hydroxyethyl methacrylate) (pHEMA) semi-interpenetrated (semi-IPN) either with polyacrylic acid (PAA) or polyvinylpyrrolidone (PVP), and loaded with tetaethylenepentamine (TEPA) for the removal of copper corrosion layers. The physico-chemical characterization of the semi-IPNs showed that alkaline pH increases the swelling of the pHEMA/PAA gels, owing to the ionization of carboxyls in PAA. In the pHEMA/PVP semi-IPN, increasing pH causes the partial formation of the PVP enolate form, changing the mesh size and macroporosity of the network. TEPA is able to interact with carboxylates in PAA and CO groups in PVP, as indicated by FTIR 2D Imaging. The interaction of the semi-IPN matrix with Cu(II) ions is stronger for pHEMA/PAA, with faster uptake kinetics; the process comprises an initial diffusion-limited stage, followed by diffusion in smaller pores or adsorption at less available sites. For the pHEMA/PVP, the uptake kinetics appears to be controlled by adsorption, as expected considering the porogen role of PVP [2]. The TEPA-loaded semi-IPNs were assessed on aged bronze mock-ups: copper oxychlorides dissolve and migrate into the gels, leaving unaltered patinas of cuprite that are valued in bronze conservation as they passivate the surface against recurring corrosion. The performance of the TEPA-loaded semi-IPNs surpassed that of traditional approaches using EDTA salts, opening new perspectives in the preservation of bronze collections.

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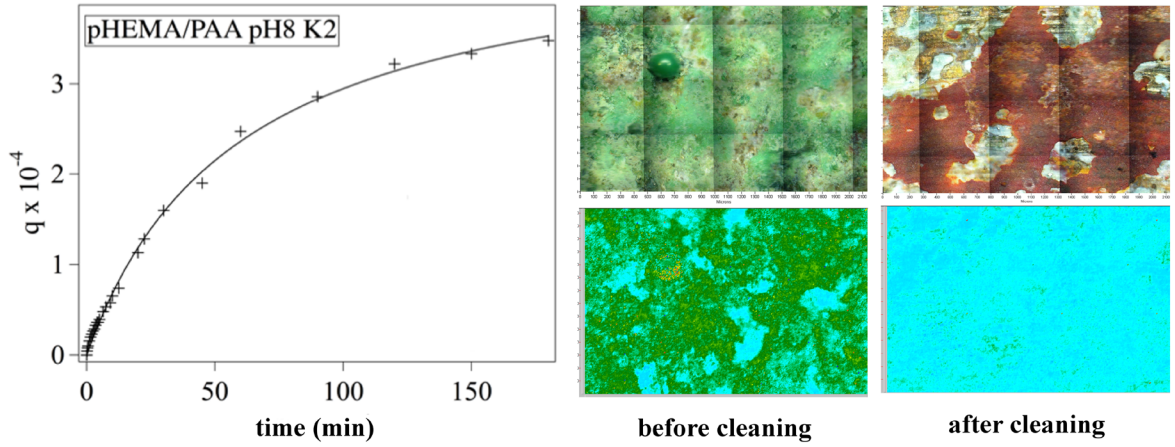
[2] N. Bonelli, G. Poggi, D. Chelazzi, R. Giorgi, P. Baglioni, *J. Colloid Interf. Sci.* **2019**, *536*, 339.



gel Cu(II) uptake kinetics **Removal of corrosion from bronze**

(Left) Cu(II) uptake (q, g/g) of a pHEMA/PAA semi-IPN at pH 8, fitted to a pseudo-second order (K2) adsorption kinetic model. **(Right)** Selective removal of green corrosion patinas from bronze using the gel, leaving unaltered the valued red cuprite layer. Top panels are Vis light images (1.5 x 2.0 mm^2). Bottom panels are IR maps of copper oxychlorides (green pixels) over the original bronze surface (azure pixels).

Electrochemical study of Smart Nanocarriers forImproved Corrosion Protection of Reinforced Concrete

Elena Messina [a], Maria Paola Staccioli [a], Cristina Riccucci [a], Marianna Pascucci [a], Monica Albini [a], Gabriel M. Ingo [a], Gabriella Di Carlo [a]

[a] Istituto per lo Studio dei Materiali Nanostrutturati-Consiglio Nazionale delle Ricerche, Area della Ricerca CNR-Montelibretti, via Salaria km 29.3, 00015 Monterotondo (RM), Italy

Chloride-induced corrosion of carbon steel reinforcement is the most important cause of premature failure on reinforced concrete structures.
This paper deals with a study was to develop smart materials with stimuli-responsive properties toward chloride-induced corrosion for the long-term protection of steel.
The use of smart nanocontainers to store corrosion inhibitors significantly increases the efficiency providing active corrosion protection [1-2].
Electrochemical techniques, measurements of corrosion potential in simulating concrete pore solution and electrochemical impedance spectroscopy (EIS) were used to determine the corrosion behavior of the specimens when a cell containing a 3.5% NaCl solution was applied on the rehabilitation mortar. Results are discussed taking into account the most likely mechanism of inhibition, in relation to the functional group of tested organic compounds
The stimuli-responsive properties and the complementary protective action of amino acid-loaded nanocontainers as a migrant corrosion inhibitors make them attractive for the long-term protection of steel and open the way for innovative solutions in the preservation of concrete cultural heritage.

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Synthesis of PeL/TiO_2 Coupled Photocatalyst for Environmental Applications Related to the Emerging Pollution

Stefano Alberti [a], Barbara Benedetti [a], Laura Romani [a], Michela Rucco [a], Marina Di Carro [a], Emanuele Magi [a], Maurizio Ferretti [a]

[a] *Department of Chemistry and Industrial Chemistry, University of Genoa, via Dodecaneso 31, 16146, Genova (GE), Italy*

The exploitation of heterogeneous photocatalysis as process intended for wastewater remediation is a topic which has been widely investigated during the last decades. The photoactivity of materials like TiO_2, triggered by irradiating with a proper wavelength, is able to generate reactive oxygen species, such as hydroxyl radical, that can easily react with organic molecules and lead to their degradation. For this reason, the use of TiO_2 for the treatment of waters and wastewater is promising towards the degradation of emerging organic pollutants that are affecting the quality of water. Nowadays, human beings need to face a new threat to their health, i.e., the emerging pollution, caused by the continuative replenishment into the environment of compounds deriving from pharmaceutical and personal care products [1]. Taking into account the high heterogeneity of the physical-chemical properties of these compounds, together with their steady insertion into the environment, it's easy to foresee the issues arising from this new kind of pollution. Indeed, not only the quality of water is affected but also the balance of the environment where thousands of microorganisms live is severely endangered. As common wastewater treatment plants are not able to degrade the pollutants belonging to this class, scientific research has put much effort in order to find a suitable way to face this threat [2].

An innovative TiO_2-based catalyst for photooxidation processes was prepared in our laboratory. TiO_2 was synthesized via a sol-gel process and later coupled with a commercial persistent luminescence "PeL" material, in order to provide a support which is also able to act as internal irradiation source [3]. To find the best synthetic conditions leading to the most effective photocatalyst, a factorial experimental design (2^3) was applied, by investigating the degradation of methylene blue used as model pollutant. The optimized sample was then tested on the degradation of a real emerging pollutant, i.e., salbutamol. Salbutamol is a β-agonist drug used for asthma treatment, which possesses rather hydrophilic properties; as it is not removed by classical wastewater treatments, it represents an appropriate case study to test the prepared photocatalyst. A photooxidation experiment was performed to investigate salbutamol degradation: a solution containing both salbutamol and the synthesized photocatalyst in water was subjected to simulated solar light irradiation and the analyte concentration was monitored over time. Several aliquots of the solution were sampled at constant time intervals and analysed by means of UV-Vis spectrophotometry. Then, salbutamol degradation was confirmed by a highly specific HPLC-MS/MS method. The results showed a rapid decrease of the pharmaceutical concentration, which was completely depleted after 2 hours. An experiment conducted in the same conditions, but without the photocatalyst, confirmed the effectiveness of the prepared material. A study based on untargeted HPLC-MS analysis for the identification of potential by-products is currently ongoing.

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EPR Spectroscopy Characterization of Melanin biomaterials: structural, dynamical and antioxidant activity insight

Maria Camilla Baratto, Maher Al Khatib, Jessica Costa, Rebecca Pogni

Department of Biotechnology, Chemistry and Pharmacy, University of Siena, Via Aldo Moro 2, 53100 Siena, Italy

Melanins are pigments naturally occurring in all species of the biological kingdoms. In humans melanins are produced by the enzymatic oxidation and polymerization of tyrosine and in lower organisms by the autoxidation of phenolic compounds [1-3]. In humans the most important form of melanin is eumelanin, an insoluble brown-black pigment. [2]. Allomelanins are a heterogeneous group of melanins including pyomelanin that is produced by the catabolism of tyrosine or phenylalanine through the activity 4-HPPD (4-hydroxyphenylpyruvic acid dioxygenase) and HGA-oxidase (homogentisic acid oxidase). Melanins show a persistent paramagnetism, antioxidant activity and conducting properties [4].

At first the research was focused on the paramagnetic properties of enzymatically produced dopa melanin and cysteinyldopa melanin using a Continuous wave (CW)-Multifrequency EPR (X- and Q-band) approach and through selective microwave pulses at Q-band frequency. The longitudinal relaxation times of the two different pigments were studied and for the cysteinyldopa melanin a faster relaxation dynamic was evident (Fig. 1) [5]. Eumelanin is an insoluble pigment while for biotechnological applications soluble melanins can have wider applications.

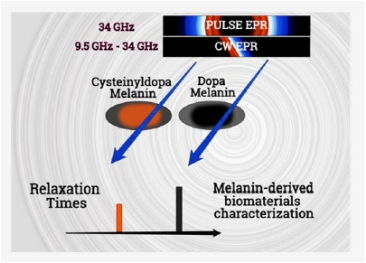

Figure. 1

In this context, pyomelanin mimics were synthesized through the oxidation of homogentisic (HGA) and gentisic acid (GA) by *Trametes versicolor* laccase at physiological pH. Due to the persistent paramagnetism of melanins, Electron Paramagnetic Resonance spectroscopy is a straightforward technique for the structural and dynamical characterization of their constituting radical species. Pyomelanin mimics have been characterized at (CW) X- and pulse Q-band (Fig.2): at least two different radical species have been detected and characterized, a carbon- and an oxygen-centered radical. The longitudinal relaxation times were determined and compared to that of eumelanin. The two pigments resulted water soluble and show a high antioxidant activity [6].

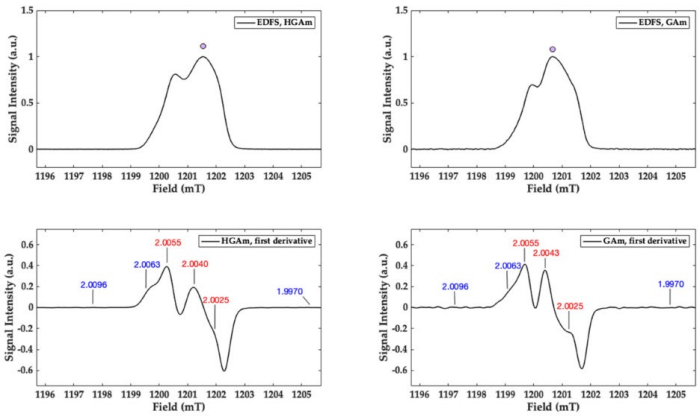

Fig. 2. Q-band (ν=33.67GHz) EPR field swept echo detected spectrum (EDFS) recorded at 298K for the HGAm sample (left panel, up) and the corresponding pseudo filed modulation spectrum calculated (left panel down) are reported and compared with the corresponding ones obtained for the GAm pigment (right panel) (ν=33.67GHz). Rectangular pulses were used for the Hahn echo sequence π-τ-π/2, with pulse lengths π=76ns and π/2=38ns. The g matrix values for the radical species are

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Regulating the magnetic properties and interactions of spinel ferrite nanoparticles via elemental doping.

Miran Baričić [a], Pierfrancesco Maltoni [b], Anna Del Tedesco [c], Gianni Barucca [d], Roland Mathieu [b], Fabio Canepa [a], Davide Peddis [a,f] and Maurizio Ferretti [a]

[a] Dipartimento di Chimica e Chimica Industriale (DCCI), Università degli Studi di Genova, Via Dodecaneso 31, Genova, 16146, Italy; [b]Department of Materials Science and Engeneering, Uppsala Universitet, Ångstromlaboratoriet, Box 35, 751 03 Uppsala, Sweden; [c]Department of Molecular Sciences and Nanosystems, Università Ca' Foscari, Venezia, 30170, Mestre, Venezia, Italy; [d]Dipartimento SIMAU, Università Politecnica delle Marche, Via Brecce Bianche, Ancona, 60131, Italy; [f]Istituto di Struttura della Materia – CNR, Area della Ricerca di Roma1, Monterotondo Scalo, Roma 00015, Italy.

Spinel ferrite magnetic nanoparticles (NPs) (MFe_2O_4; M = Fe^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} etc.) are a class of inorganic materials studied for their magnetic properties and biocompatibility. Their structure hosts cations in tetrahedral (A) and octahedral (B) interstices, and the cationic distribution (*i.e.*, inversion degree) among them can heavily change the resulting magnetic properties. Experimental factors like thermal history, surface effects or synthesis method have a large influence on the inversion degree and magnetic properties and require control for a precise study[1], [2]. Chemical engineering of the magnetic properties has been performed by changing M^{2+} cation composition[3], [4].

In this work, a set of ~ 9 nm roughly spherical zinc-cobalt ferrite NPs ($Zn_xCo_{1-x}Fe_2O_4$, x from 0 to 0.48) was synthetized by thermal decomposition of organometallic precursors [5]. Spinel ferrites´ phase formation, size and shape were confirmed by means of a morphological-structural characterization (*i.e.*, X-Ray Powder Diffraction, Transmission Electron Microscopy).

Field dependent magnetization loops at 5 K displayed an increase of saturation magnetization (M_S) and a decrease of anisotropy, when Zn^{2+} fraction increases. This was furtherly confirmed by ZFC/FC protocols. Nevertheless, the trend in M_S at 5 K is not respected at 300 K, owed to Zn^{2+} effect on the magnetic order resistance to thermal agitation. A better understanding on the process was achieved by measuring the magnetization dependence upon temperature. Eventually, magnetic interparticle interactions were studied by remanence plots (*i.e.*, DCD and IRM). All the plots show a downward shifting of the negative peak position and intensity with increasing x, pointing out a strong effect on demagnetizing interactions. This opens the way for the application of Random Anisotropy Model in order to investigate the magnetic anisotropy and interparticle interactions. [6], [7].

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Porous carbons derived from plastic waste for the capture of CO_2

Federico Begni[1], Vanessa Miglio[1], Chiara Bisio[1,2], Enrico Boccaleri[1], Geo Paul[1] and Leonardo Marchese[1]

[1] Dipartimento di Scienze e Innovazione Tecnologica, Università degli Studi del Piemonte Orientale" Amedeo Avogadro", Viale Teresa Michel 11, 15121-Alessandria (Italy);[2]CNR-SCITEC Istituto di Scienze e Tecnologie Chimiche "G. Natta", Via C. Golgi 19, 20133-Milano (Italy).

Porous carbons are normally obtained via pyrolysis of organic species. The textural properties, and the very high physico – chemical stability, allow porous carbons to be employed in a vast number of applications such as gas storage, pollutants removal, membrane separation, photochemical catalysis such as CO_2 and O_2 reduction, energy storage and as electrode materials for batteries, fuel cells and supercapacitors[1]. The carbonization process allows the formation of the porous structure, usually both micro- and mesoporous in nature. The extreme conditions at which carbons are formed allow to choose from numerous precursors and in fact porous carbons have been prepared even from food waste[2] or plant - based starting materials[3]. Since choices can be made regarding the precursor, one possible strategy is to select low – value starting materials which can then be transformed via inexpensive processes into porous carbons. One possibility is represented by plastic wastes which are among the most abundant and still represents a problem in terms of recycling technologies. In this work, we report the synthesis and characterization of porous carbons derived from plastic wastes of different origin. Indeed, the objective of the work is to recover all the polymers from the treatment of the organic fraction of municipal solid waste, to separate them and to enhance the different fractions in a sustainable way.

In particular, plastic objects such as drinking bottles and other plastic wastes have been recovered, characterized and separated into the main polymeric fractions, namely polyethylene, polypropylene and polyethylene terephthalate. Porous carbons have been obtained from each polymeric fraction via chemical activation with KOH at 800 °C and were fully characterized via SEM microscopy, Raman spectroscopy and N_2 physisorption analysis. In addition, the CO_2 adsorption capacities were tested using a prototypal apparatus. CO_2 adsorption capacities were then compared to those of commercial porous carbons. Preliminary results confirmed the fairly high adsorption capacities of the resulting porous carbons. In particular CO_2 adsorption capacities for unfunctionalized porous carbons are usually found to be around 3 mmol g^{-1} at 25 °C[4]. Here, as reported in figure 1, the value of 2.5 mmol g^{-1} at 25 °C was found for the porous carbon derived from PET bottles.

This work has been done in the frame of the Saturno Project "*Biorefinery for the conversion of organic waste and CO2 into biofuels, bio-fertilizers and biochemical*" funded by the Piedmont Region and aiming at the conversion of urban organic waste into raw materials for use in various sectors (industrial and waste chemicals, fuels and automotive, agriculture, biochemistry and industrial and cement-based biotechnologies) and at the recovery and conversion of CO_2 through the development, application and validation of innovative methodologies.

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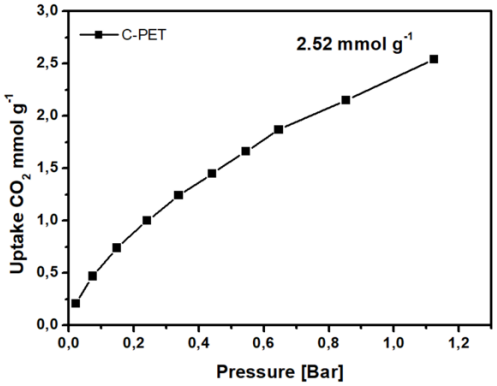

Figure 1. CO_2 adsorption isotherm up to 1 bar at 25 °C on the porous carbon C-PET derived from PET waste.

Impact of substituent orientation on the excited state deactivation pathways of phenothiazine-based isomers showing aggregation-induced emission

Tommaso Bianconi[a], *Pietro Mancini*[a], *Rajneesh Misra*[b], *Benedetta Carlotti*[a]

[a] *Department of Chemistry, Biology and Biotechnology, University of Perugia, Perugia 06123, Italy;*[b] *Department of Chemistry, Indian Institute of Technology Indore, Indore 453552, India*

Most traditional light-emitting materials suffer from the low solubility in water and the Aggregation-Caused Quenching (ACQ) effect in high concentration solutions or in the solid state due to the π- π interactions. The Aggregation-Induced Emission (AIE) phenomenon [1], discovered by Tang et al. in 2001, offers a straightforward remedy to all these issues. Typical AIE-based fluorophores are characterized by propeller-shaped rotor-like structures, which undergo low energy torsional and vibrational motions as isolated molecules and emit very weakly in solution. Conversely, their aggregates, produced in water dispersions or in the solid state, show strong emission which is generally attributed to the restriction of intramolecular motions (RIM) in the aggregate state. This unique feature of AIE-based systems provides a new platform for the development of fluorescent probes for analyte sensing and imaging. The excited state mechanism underlying this interesting emissive behavior remains still unclear. In this light, the aim of our research was the investigation of the photo-physical properties of three phenothiazine-based isomers [2] (Fig. 1).

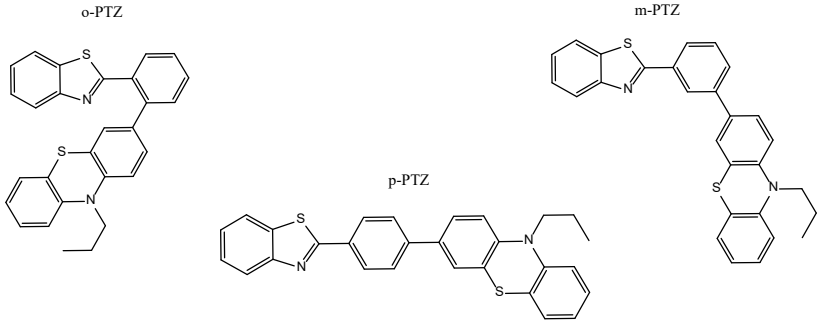

Figure 1. Molecular structures of *ortho*, *meta* and *para* isomers labelled as *o*-PTZ, *m*-PTZ and *p*-PTZ, respectively.

Specifically, in this work, these compounds were investigated in a wide set of organic solvents, in water dispersion and in solid state to evaluate the impact of the medium on the emission phenomena and on the processes that compete with the radiative deactivation, such as intramolecular charge transfer (ICT) and inter system crossing (ISC). This study was carried out by means of stationary and time-resolved absorption, fluorescence and phosphorescence spectroscopy. In particular, advanced spectroscopic techniques, such as nanosecond and femtosecond transient absorption and femtosecond broadband fluorescence up-conversion, were employed to follow the dynamics of the lowest excited singlet and triplet states.

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Dynamical features of the active state of the SHP2 oncoprotein and their implication in the allosteric regulation mechanism: insights from REMD simulations

Gianfranco Bocchinfuso, Valerio Santucci, Paolo Calligari, Lorenzo Stella

Department of Chemical Science and Technologies, University of Rome Tor Vergata, 00133 Rome, Italy;

The Src homology-2 domain-containing phosphatase 2 (SHP2) mediates signal transduction downstream of various receptor tyrosine kinases (RTKs). This protein was the first tyrosine phosphatase for which an oncogenic role was demonstrated [1]. In addition, SHP2 activity is required for survival of receptor tyrosine kinases (RTK)-driven cancer cells, it is involved in intrinsic and acquired resistance to targeted cancer drugs, it mediates activation of immune checkpoint pathways and it is involved in the induction of gastric carcinoma by *H. pylori*. For all these reasons, SHP2 is a central target in cancer therapy [2].
From a structural point of view, SHP2 comprises two Src homology 2 (SH2) domains, called N-SH2 and C-SH2, followed by the catalytic protein tyrosine phosphatase (PTP) domain, and a C-terminal tail. SH2 domains are recognition elements that bind protein sequences containing a phosphorylated tyrosine (pY) [3]. In particular, the N-SH2 domain blocks the active site on the PTP domain in the inactive conformation and it is involved in the interaction with other proteins, determining the right compartmentalization of the protein in its active state [4]. These two different functions of N-SH2 domain are coupled, with the affinity for the molecular partners that increases when N-SH2 is detached from the PTP active state. [5]. This coupling is crucial in the SHP2 regulation mechanism, but the structural details of these allosteric changes are debated. Essentially two different allosteric mechanisms have been proposed, evoking the role of the EF loop close to the N-SH2 binding site [6] or the features of two β-strands in the core of the domain [7].
For the first time, we performed Replica Exchange Molecular Dynamics (REMD) simulations on the SHP2 active state, starting from a recently reported crystallographic structure (pdb code 6crf [8]). Our simulations return a view of a flexible active state, in which an ensemble of conformations concurs to the global properties of the protein. Furthermore, they shed new light on the N-SH2 allosteric conformational transitions which are the basis of the SHP2 regulatory mechanism and reveal a previously unreported role of the BG loop.

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A comprehensive study of nanoparticles protein corona formation in a mimicked blood flow physiological environment

Beatrice Lucia Bona, Martina Colombo, Cindy Cardenas Rincon, Roberto Rusconi, Francesco Cellesi, Pierangelo Metrangolo and Francesca Baldelli Bombelli

[a]*Department of Chemistry, Materials and Chemical Engineering, Politecnico di Milano, Milano, Italy.* [b]*IRCCS Humanitas Research Hospital, Rozzano, Italy.*

In the field of nanomedicine, a deep understanding of nanoparticles (NPs) biological identity and mechanisms driving NPs interaction with cell membrane, is crucial for the design of safer and more efficient delivery systems as well as to predict possible toxicity effects. Mainly administered through systemic injection, NPs, ones in contact with the biological fluids, are immediately coated with two layers of environmental proteins, respectively called the hard corona (proteins strongly bounded) and the soft corona (proteins loosely associated). Protein corona complexes represent the real nano-interface interacting with the cell membrane, providing a new "biological identity" to NPs, able to completely change the way NPs interact with cells (i.e PC can slow down NPs degradation kinetic, modify their biodistribution and cellular uptake and affect the inflammation signaling).[2,3] Understanding PC formation and characterizing its composition in dependence of the physicochemical properties of the NPs and dynamic bloodstream environment is thus essential to understand NP *in vitro* and *in vivo* behavior.[1] However, to date, most of the reported studies on NP PC have been carried out in static conditions, without considering the high influence the dynamic nature of physiological environment has on protein corona formation and composition.
Here we developed a successful method to study the behavior and the biological identity of a library of innovative theranostic PCL-PEG based NPs, under physiological blood flow conditions, using a microfluidic system. This method allows to efficiently isolate and characterize NP protein corona, unraveling the interplay of size and NP composition on their biological identity in the dynamic conditions of blood flow.

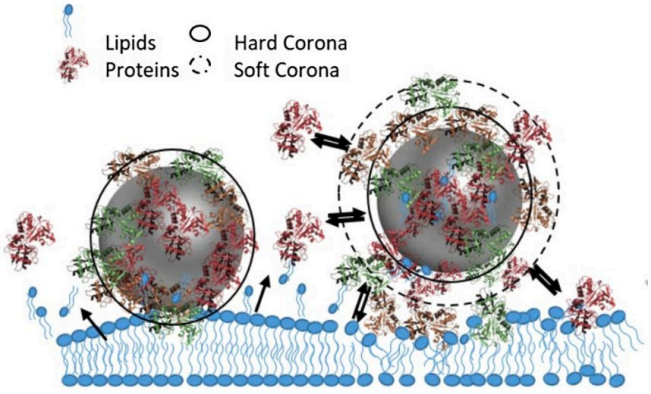

***Figure 1**. Schematic representation of the complex series of interactions between environmental proteins and NPs and then between PC-NPs and the cell membrane. Figure readapted from [4]*

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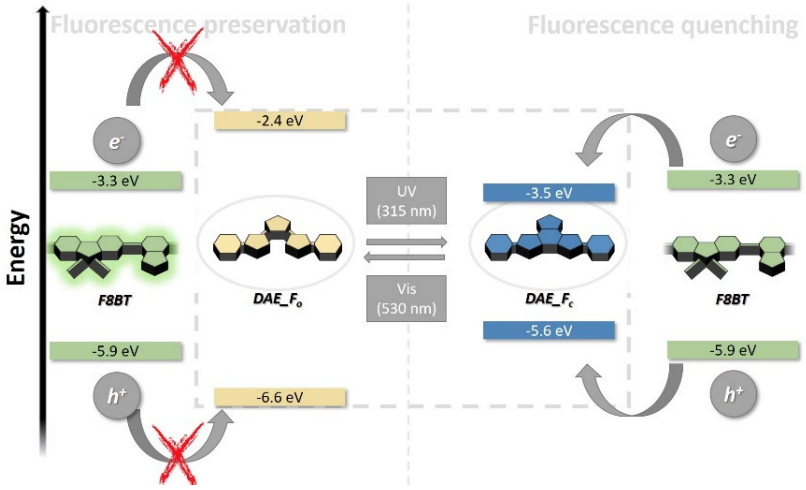
Modulation of Charge Carriers Trap States of Optically Switchable OLEDs

Aurelio Bonasera,[a,b] Giovanni F. Cotella,[c] Alessandro Minotto,[c] Giuseppe Carnicella, [c]Stefan Hecht,[b,d] Franco Cacialli[c]

[a]Dept. of Physics and Chemistry - Emilio Segrè, University of Palermo, and INSTM - Palermo Research Unit, Palermo, Italy; [b]Institut für Chemie & IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany; [c]Dept. of Physics and Astronomy and London Centre for Nanotechnology, Bloomsbury-London, United Kingdom; [d]DWI - Leibniz-Institut für Interaktive Materialien and RWTH Aachen Institut für Technische und Makromolekulare Chemie. Aachen, Germany.

Organic Light-Emitting Diodes (OLEDs) represent a success in the market of lighting technologies, due to their appealing brightness, elevate emission quantum efficiency, and compatibility with printing approaches on flexible substrates.[1] Emerging interest goes around responsive materials to be integrated in these devices, to remotely control the device performance by means of external stimuli, such as light.[2] In this scenario, photochromic compounds are highly attractive, and diarylethenes (DAEs) possess (i) vastly different optical, and energetic properties between the two thermally stable isomers,[3] (ii) high isomerization reversibility and fatigue resistance,[4] (iii) versatile synthetic protocols, allowing precise tuning of the molecular properties.[5] Here we report the successful design, fabrication and characterization of Optically Switchable OLEDs (OSOLEDs) combining the commercially available F8BT emitting polymer and a specifically designed DAE-derivative. Following UV-Visible and photoluminescence spectroscopy investigation of the selected DAE molecule in solid state, F8TB:DAE blends are prepared considering different dopant loadings; the best performing device (5 wt.% loading) returns a maximum reversible and optically induced threshold voltage (Vth) shift of 2.9 V with a maximum current density and luminance ON/OFF ratio of ~ 20 and ~ 90, respectively. The impact of the DAEs isomerization on the charge carriers has been separately investigated, for the first time, via the design, fabrication, and characterization of single-carrier switchable devices, proofing that the electrons transport is more affected by DAE optical switching as electron-only devices show the largest current variation upon irradiation.



[1] B. Geffroy *et al.*, *Polym. Int.* **2006**, *55* (*6*), 572.
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Microfluidic effect of viscosity gradient on diffusivity of nanoparticles flowing in laminar regime

Federico Calì, [a] *Nunzio Tuccitto*, [a,b] *Luca Fichera*, [a] *Giovanni Li-Destri*, [a-b] *Grazia M. L. Messina*, [a] *Antonino Licciardello* [a,b] *and Giovanni Marletta* [a,b]

a) Department of Chemical Sciences, Università degli Studi di Catania, Viale A. Doria 6, 95125 Catania, Italy.
b) Laboratory for Molecular Surfaces and Nanotechnology-CSGI, Viale A. Doria 6, 95125 Catania, Italy

Molecular communication is an alternative communication approach in which chemicals are used as messengers. Just as in biological systems, which have always used molecules or molecular aggregates to communicate, an artificial platform for molecular communication consists of a transmitter that enable the message to be encoded, a communication channel in which a carrier fluid transports the messengers, and a receiver that enables decoding. [1] We will present our recent findings about the investigation of the effect of viscosity gradients in the carrier fluid on the flowing of suspension of fluorescent carbon nanoparticles used as chemical messengers under microfluidic conditions. Firstly, we have simulated the information transport process by numerically solving the governing differential equation. It has allowed us revealing a peculiar phenomenon that occurs at the interphase between two miscible liquids having different viscosities, namely: water and glycerol. Then, we have undertaken an intensive experimental campaign by using a prototypal artificial molecular communication platform we made on purpose in our laboratory. With the vast number of hence obtained signals, it was possible to validate the theoretically predicted findings.

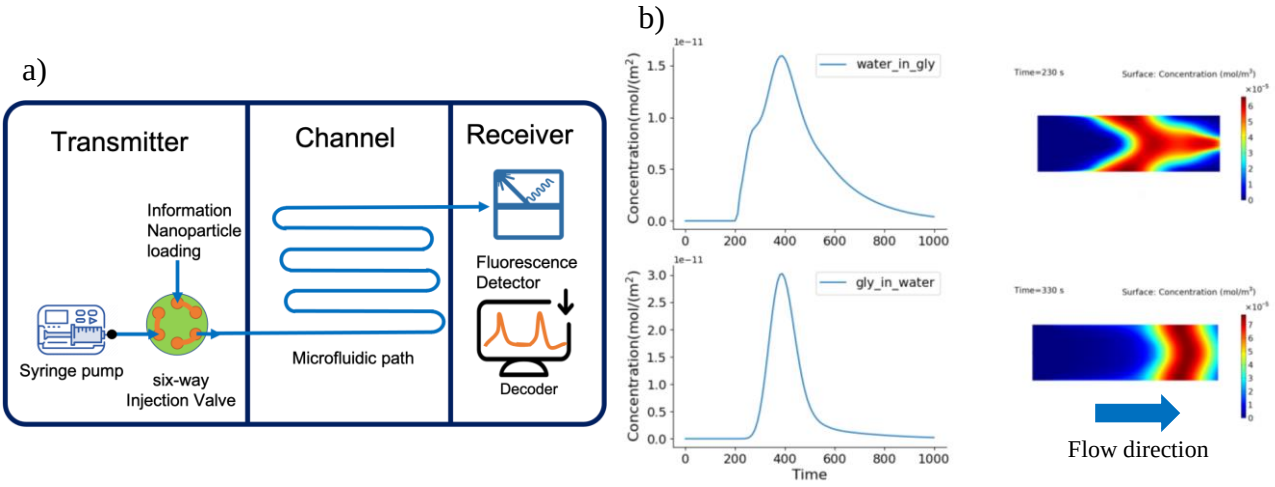

Figure 1. a) Schematic representation of the MoCo prototypal platform [2]; b) Simulated results of the transport of molecular messengers under different viscosity conditions between the carrier and the substance injected plug.

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Plasmonic effect on amyloid fibrils disaggregation

Elena Cambiotti[a], Giulia Quaglia[a], Eva Bystrenova[b], Zuzana Bednarikova[c], Andrea Antosova[c] Paola Sassi[a], Francesco Valle[b], Zuzana Gazova[c] and Loredana Latterini[a]

[a] Department of Chemistry, Biology and Biotechnology, University of Perugia, Italy; [b] Institute of Nanostructured Materials ISMN - CNR, via Gobetti, 101, 40129 Bologna, Italy; [c] Institute of Experimental Physics, Slovak Academy of Science, Watsonova 47,043 53 Kosice, Slovakia

The interaction between gold nanoparticles and amyloid fibrils achieves great attention for the prevention and treatment of various neurodegenerative disorders including Alzheimer's disease, Parkinson's disease and amyotrophic lateral sclerosis (ALS), all of which represent a major health issue in today's world.[1] The mechanisms leading to amyloid diseases are due to a conformational change of native proteins resulting in the aggregation and formation of insoluble amyloid fibrils which are deposited and accumulated on biological tissue. The disruption or disaggregation of these insoluble species might be an efficient therapeutic strategy to treat the amyloid disease. One tool to inhibit fibril formation is nanotechnology[2]: recent studies are demonstrating that conformation of protein aggregates is altered when binding to nanoparticles[3,4].

In this work, spherical gold nanostructures (Figure 1a) having 23 and 45 nm diameters, and 23x45 nm nanorods (Figure 1b), both functionalized with citrate, have been synthesized following different strategies to investigate the effect of size and morphology of nanomaterials on the disaggregation process. The irradiation of metal nanomaterials at selected wavelengths induces the excitation of the plasmonic absorption and activates either a photothermal effect [5,6] or the production of ROS species,[7,8] which can be exploited to induce an effect on fibril stability and a more efficient depolymerization. Changes in the structure and morphology of amyloid fibrils have been studied through UV-Vis, Fluorometric, ATR-IR spectroscopy and AFM and TEM microscopy. Gold nanostructures taken into account are able to damage the amyloid conformation; the results are discussed in terms of shape and size of colloid nanoparticles.

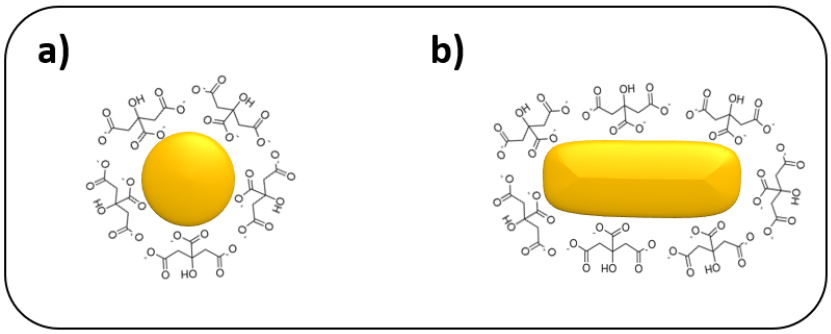

Figure 1 Representation of gold nanospheres (a) and gold nanorods (b) stabilized on the surface by citrate

References:

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Emissive 2D Mn - based Hybrid Metal Halides

Marta Campolucci[a, b], Emanuela Sartori[a, b], Liberato Manna[b], Federico Locardi[a, b], Maurizio Ferretti[a]

[a]Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy; [b]Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

In the last decade, the research on lead halides perovskite (LHP) $APbX_3$ ($A = CH_3NH_3^+$, Cs^+; $X = Cl^-$, Br^-, I^-) has revolutionized the field of colloidal semiconductor nanocrystals. LHPs exhibit excellent properties in view of photovoltaic (PV) applications, or in industrial use [1]. In general, a halide perovskite crystal lattice has a cubic structure with a general ABX_3 (or equivalent) stoichiometry. In particular, LHPs are formed by 3D interconnected $[PbX_6]^{4-}$ octahedra, with the A-site cation residing in the large voids in between. Yet, deviations from this ABX_3 stoichiometry can be obtained when the A and B cation sites become partially or fully vacant, or when they are replaced by a combination of other cations. In particular, larger or smaller cations favor the formation of polymorphs of a lower dimensionality (2D or 0D), with octahedra less connected or completely isolated. These 2D and 0D structures are better defined as metal halides since they don't retain the classic perovskite structure [2]. The insertion of an organic cation instead of an inorganic one dramatically changes other properties, such as the conductivity and the transport properties, fundamental features required for application as PV. Promising compounds can be obtained starting from the emissive Mn-based stoichiometries $AMnX_3$ and A_3MnX_5. In fact, $CsMnBr_3$ crystals are lead-free and red-emitting, with a high PLQY [3]; Cs_3MnBr_5 crystals show a narrow band green emission peaking at 520 nm with PLQYs around 50% in bulk [4].

Here, we present the recent results achieved in the preparation of emissive 2D Mn-based hybrid metal halides single crystals, where Cs^+ cation is replaced by butylammonium BA ($C_4H_{12}N^+$). The prepared materials show red and bright orange emission, respectively for $BAMnBr_3$ and BA_3MnBr_5. The synthesis used is based on the evaporation of the solvent in acid medium, starting from bromide salts. The characterization of these materials is made using techniques such as XRD, FTIR, DTA-TG coupled with GC-MS. New hybrid phases with interesting optical properties have been produced, suitable for optoelectronic applications, such as LEDs.

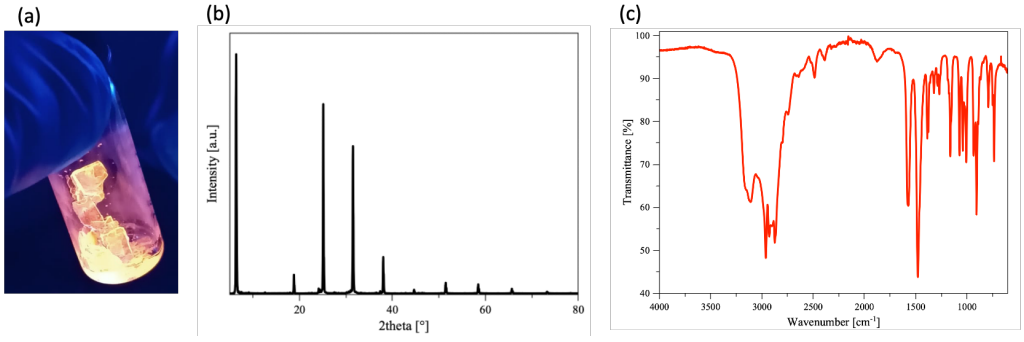

Figure: (a) Emission under UV excitation (b) XRD pattern and (c) FTIR spectrum of BA_3MnBr_5 single crystals.

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2D Ruddlesden-Popper Perovskites $BA_2MA_{n-1}Pb_nI_{3n+1}$ as studied by Solid-State NMR Spectroscopy

Elena Maurina[a], Noemi Landi[a], Elisa Carignani[b], Silvia Borsacchi[b,c], Lucia Calucci,[b,c] Daniela Marongiu[d], Michele Saba[d], Marco Geppi[a,b,c]

[a]Department of Chemistry and Industrial Chemistry, University of Pisa, via G. Moruzzi 13, 56124 Pisa, Italy; [b]Institute for the Chemistry of OrganoMetallic Compounds, Italian National Council for Research, CNR/ICCOM, via G. Moruzzi 1, 56124 Pisa, Italy; [c]Center for Instrument Sharing, University of Pisa (CISUP), 56126 Pisa, Italy; [d]Department of Physics, University of Cagliari, S.P. Monserrato-Sestu Km. 0700, Monserrato, 09042 CA, Italy

Lead Halide Perovskites are interesting semiconductors used in different optoelectronic devices (e.g. sensitizers for solar cells, photodetectors, LEDs). Recently, 2D analogues of Hybrid Lead Halide Perovskites (HLHP) have attracted considerable attention because they offer the possibility of tunable band gap and enhanced environmental stability with respect to the corresponding 3D systems. 2D Ruddlesden–Popper (RP) perovskites can be prepared by adding a large organic mono ammonium cation L^+ in the precursor solution. In this way the 3D structure of corner-sharing octahedra (ABX_3) is disrupted and a structure with a bilayer of spacer cations between metal halide sheets is formed ($L_2A_{n-1}B_nX_{3n+1}$). For example, butylammonium (BA) is a suitable organic cation to force the archetypical perovskite $MAPbI_3$ into 2D RP perovskites $BA_2MA_{n-1}Pb_nI_{3n+1}$ (Figure 1), which are the object of the present study. The layer thickness of metal halide sheets is specified by n and can be adjusted by tuning precursor stoichiometry.

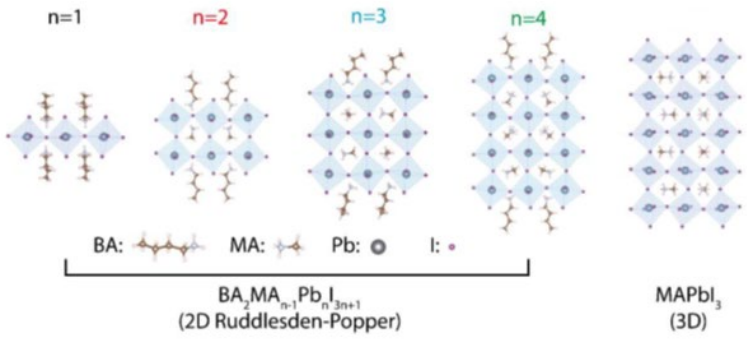

Figure 1. Schematic structure of 2D RP perovskites $BA_2MA_{n-1}Pb_nI_{3n+1}$ for n=1, 2, 3, 4, and of the corresponding 3D perovskites $MAPbI_3$.

Solid-State NMR stands out as characterization technique for HLHP for its ability to study ion dynamics, compositional variations and ion incorporation, chemical interactions and degradation mechanisms [1,2]. In this work, the 2D RP perovskites $BA_2MA_{n-1}Pb_nI_{3n+1}$ with n=1, 2, 3 have been characterized by Solid-State NMR and compared with 3D $MAPbI_3$ as a reference compound. The structural features of these systems have been investigated by ^{207}Pb, ^{1}H, and ^{13}C spectra recorded under Magic Angle Spinning and static conditions; the obtained results have been discussed also by comparison with very recent literature [3]. In addition, the variable temperature measurement of ^{13}C and ^{1}H spin-lattice relaxation times (T_1) allowed dynamic properties of the organic cations in the series of samples to be investigated.

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Pore size from N_2 adsorption isotherm in mesostructured siliceous materials. BJH or DFT model? GCMC/MD simulations answer the question

Paola Carta, Claudio Cara, Carla Cannas, M. Andrea Scorciapino

Department of Chemical and Geological Science, University of Cagliari, Italy (Cittadella Universitaria di Monserrato, S.P. 8 km 0,700 – 09042 – Monserrato (CA))

N_2 physisorption is the experimental method to determine surface area (SA) in porous and non-porous materials, and pore size (PS) and pore size distribution (PSD) in micro and mesoporous materials (with pores up to 50 nm). In mesoporous materials (with pores from 2 to 50 nm) Barrett-Joyner-Halenda (BJH) method and more recently Density Functional Theory (DFT) model are used to estimate PS and PSD from N_2 adsorption-desorption isotherms. BJH is the most employed method, because easily applied to a great variety of materials and no information about the pore shape is required. Mesostructured siliceous materials, offers the possibility to compare the two models, being the pores ordered and the structure well know. Among the highly ordered mesostructured silicas, we selected MCM-41 due to the 2D-pore structure P6mm (mesochannels). Transmission Electron Microscopy (TEM), Small Angle X-Ray Diffraction (SA_PXRD) and ^{29}Si Solid-State NMR were combined to N_2-phisisorption measurements to extract information about pore size, pore structure, pore wall thickness and $Q_2/Q_3/Q_4$ sites. Starting from the two pore size values obtained through BJH (PS_{BJH}) and DFT (PS_{DFT}) models on the experimental N_2-isotherms of MCM41 we propose two computer models at the atomic level to reconstruct these isotherms, combining GCMC and MD simulations. Although pore size difference between PS_{BJH} and PS_{DFT} is about 1 nm, large difference is observed in the gas adsorption isotherms. Saturation of the pore surface and the progressive formation of additional gas layers, as well as the eventual condensation, occur at a relative pressure that strongly depends on the pore size. The simulations of other gases and their mixtures bolster such dependence, with potential impact on selectivity.

Jin Shofu starch-based colloidal hydrogel dispersions for the consolidation of paintings

Andrea Casini[a,b], David Chelazzi[a,b], Rodorico Giorgi[a,b]

[a] Department of Chemistry "Ugo Schiff" University of Florence, I-50019 Florence, Italy; [b] Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase (Center for Colloid and Surface Science), University of Florence, I-50019 Florence, Italy

The preservation of brittle and fragile paint surfaces is undoubtedly one of the most significant issues in contemporary and modern art, both for their technical and optical properties, as well as their aesthetic values. Artists' unfettered experimentation with painting techniques and additive-rich paint formulations have led to artworks with weak powdering surfaces, exacerbated by severe climatic conditions and outdoor pollution. Furthermore, current conservation practice lacks suitable consolidation procedures, and traditional consolidant can result detrimental as optical properties and water permeability of the treated surfaces are dramatically altered [1].
In order to enhance penetration into porous paint layers, while avoiding optical modifications, we developed a novel starch-based nanostructured consolidant; the high surface area of the starch nanoparticles (SNPs) is rich with -OH groups, boosting pigment adhesion [2-3].
Dispersions of nano-sized starch hydrogels were obtained by precipitating gelatinized gluten-removed wheat starch (Jin Shofu) in a nonsolvent [2], and then re-dispersing the SNPs in water or water-ethanol blends. Their consolidating efficacy was satisfactorily tested on aged painted mock-ups that resemble modern painting surfaces, and followed by means of 2D (FTIR) Imaging. Pigment cohesiveness was improved while the painted layer's original optical properties were preserved.
Overall, SNPs represent a valid example where the formulation of colloidal systems from biopolymers and renewable sources can improve the resiliency of Cultural Heritage to degradation processes, favoring the transfer of works of art to future generations.

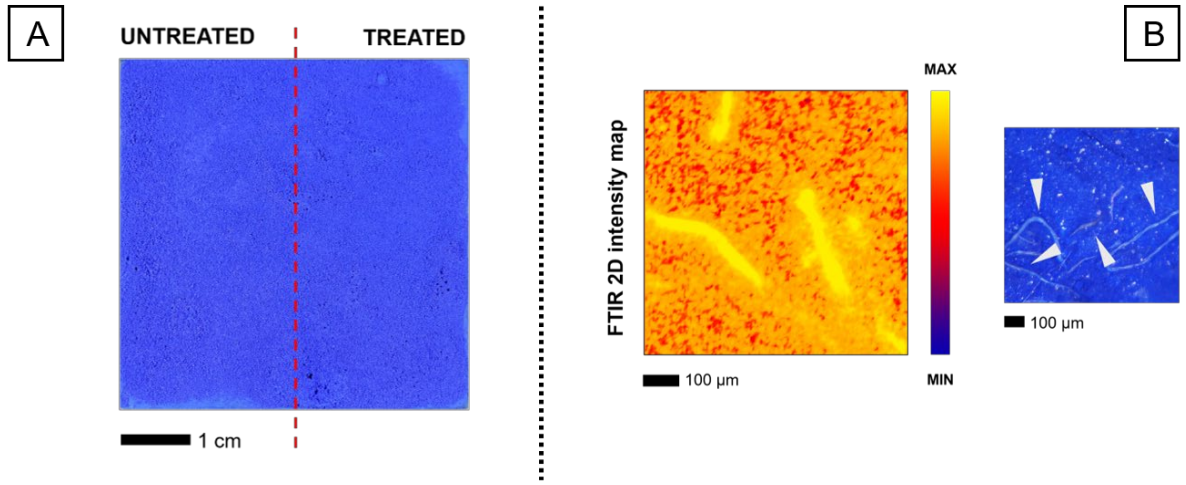

Figure. (A) Comparison between treated and untreated surface after the application of SNPs (5 g/L) to an artificially aged painted mock-ups that mimic a fragile and powdering painting surface. (B) 2D FTIR Imaging (false color) of starch distribution onto the treated mock-up' surface. Starch nano-hydrogel particles distribute homogeneously and fill cracks in the degraded painted matrix, providing reinforcement acting as micro-junctions and preserving the original paint layers' optical properties.

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Theoretical modelling of the UV and CD spectra of L-alanine in water

Cheng Giuseppe Chen,[a] Mauro Giustini,[a] Anita Scipioni,[a] Andrea Amadei,[b] and Marco D'Abramo[a]

[a]Department of Chemistry, Sapienza University of Rome, Rome, Italy; [b]Department of Chemical Sciences and Technology, Tor Vergata University, Rome, Italy.

In the present work an advanced theoretical-computational approach to model the UV absorption and the electronic circular dichroism (CD) spectra of the smallest chiral amino acid in water solution is presented. By combining quantum-mechanical calculations with molecular dynamics simulations within the framework of the MD-PMM[1, 2] QM/MM[3] method, the electronic properties of L-alanine (L-Ala) in solution at different levels of protonation are obtained while accounting for the dynamic effects of the solvent on an atomistic level. As observed in other works[4-6], the electronic properties of L-Ala display a remarkable dependence on the conformation of the molecule which needs to be properly accounted for in the calculation in order to obtain accurate results. Our method allows an extensive and appropriate sampling of the conformational space of the amino acid (see Figure) with low computational effort, therefore achieving a quantitative agreement between the model and the experiments. The accuracy in reproducing both the CD and the UV spectra makes the present approach able to provide a structure-based interpretation of the experimental signal as obtained from absorption and CD spectroscopies, the typical techniques used to investigate molecular structures in solution, and the low computational cost makes it suitable to be applied to the study of more complex systems.

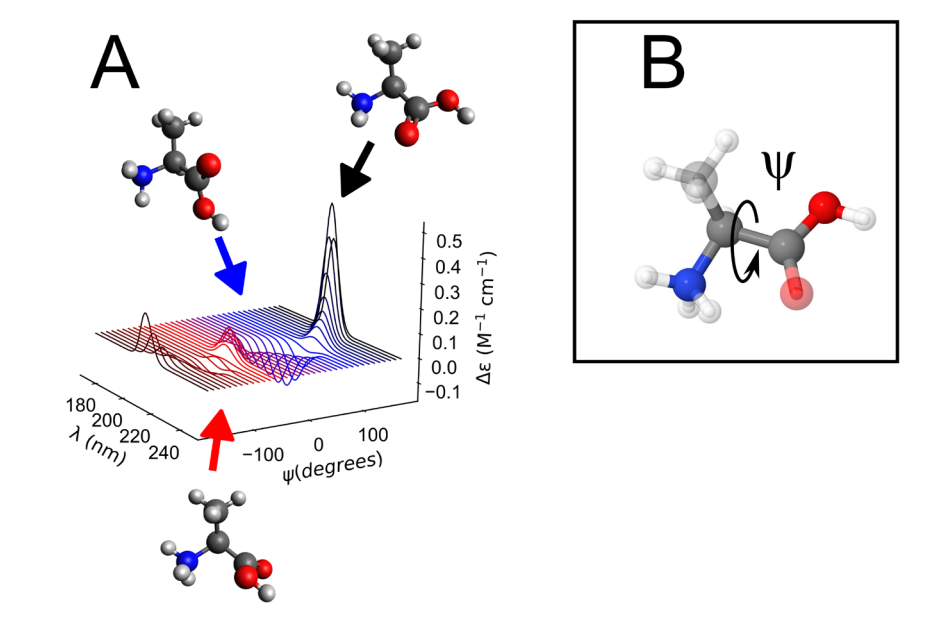

Figure: A) Calculated CD spectra of L-Ala in the cationic form in water at different values of the ψ dihedral angle. B) Definition of the ψ dihedral angle.

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Diffuse reflectance infrared assessment of nearly free silanol species on quartz surface to elucidate silica membranolytic activity

Giuseppe Chilla [a], Erica Rebba [a], Rosangela Santalucia [a], Lorenzo Mino [a, b], Chiara Bellomo [a], Cristina Pavan [a, c], and Francesco Turci [a, c]

[a]Dipartimento di Chimica, Università degli Studi di Torino, via P. Giuria 7, 10125, Torino, Italy [b]Nanostructured Interfaces and Surfaces (NIS) Interdepartmental Centre, University of Turin, Italy [c]"G. Scansetti" Interdepartmental Centre for Studies on Asbestos and Other Toxic Particulates, University of Turin, Italy

Inhalation of silica particles can induce inflammatory lung reactions that lead to silicosis and/or lung cancer. The surface of this material is studded with several silanol units. Some of us recently demonstrated that a specific subpopulation of the surface silanols, namely "nearly free silanols" (NFS), whose distance is ranging from 4 to 6 Å, are critical in initiating inflammatory responses to silica and might account for its toxic effects. Ball milling introduces NFS on the surface of quartz and the presence of NFS correlated with cell membrane damage, and *in vitro* and *in vivo* toxicity of silica.[1] The aim of this work is to validate the relevance of NFS for silica toxicity considering a larger set of pristine and modified silica samples. To overcome scattering induced by the size of quartz powders, surface silanol families were described by Diffuse Reflectance Infrared Fourier-Transform (DRIFT) spectroscopy. In order to observe surface silanols, molecular water adsorbed on the silica surface was removed, and isotopic exchange of OH with OD was carried out to discriminate surface from intra-globular silanols. Surface Si-OH (3800-3100 cm^{-1}) were readily converted into Si-OD (2800-2200 cm^{-1}). Different silanol families were detected and assigned according to the well-established frequency ranges in the OD domain: isolated (~2761 cm^{-1}), weakly H-bond interacting (2758-2720 cm^{-1}; NFS ~2757 cm^{-1}), and strongly H-bond interacting (2720-2250 cm^{-1}) silanols.[1] To gain semi-quantitative insight on the relative amount of silanol families, the spectra were normalized, converted in Kubelka-Munk units, and analysed following the approach proposed by Carteret.[2] We observed that thermal treatments ranging between RT and 350 °C modified the relative population of silanol families as a consequence of inter-silanols condensation. Specifically, by heating quartz at increasing temperature we observed a progressive increase in the relative amount of NFS (Fig. 1A), which paralleled the trend observed in the membranolytic ability of heated quartz (Fig. 1B). These results corroborate the key role of quartz surface state, and specifically the amount of NFS, in triggering membrane damage, the early biochemical event that leads to silica pathogenicity.

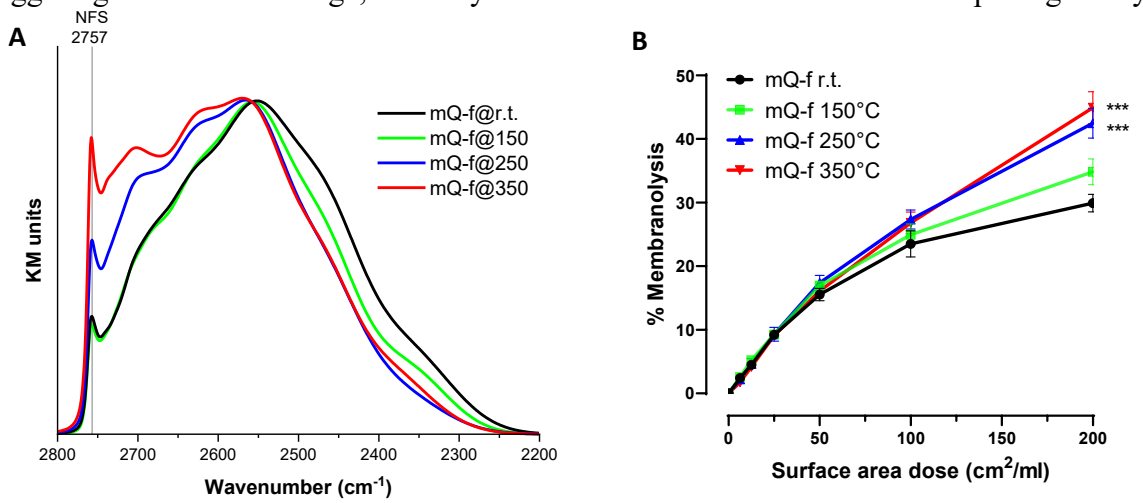

Figure 1: A) DRIFT spectra and B) membranolytic activity of quartz heated at different temperatures.

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A new methodological approach to correlate protective and microscopic properties by Soft X-Ray Microscopy and Solid State NMR Spectroscopy: *the case of Cusa's stone*

Veronica Ciaramitaro [a], Alberto Spinella [b], Francesco Armetta [a], Scaffaro Roberto [c], Emmanuel Fortunato Gulino [c], George Kourousias [d], Alessandra Gianoncelli [d], Eugenio Caponetti [a,e], Maria Luisa Saladino [a]

[a]Department of Biological, Chemical, and Pharmaceutical Sciences and Technology (STEBICEF), University of Palermo, Viale delle Scienze Bld.17, I-90128 Palermo (Italy) [b]Advanced Technologies Network (ATeN) Center, University of Palermo, Viale delle Scienze Bld.18, I-90128 Palermo (Italy) [c]Department of Engineering, University of Palermo, Viale delle Scienze Bld. 6, I-90128 Palermo (Italy) [d]Elettra - Sincrotrone Trieste, Strada Statale 14 - km 163,5 in AREA Science Park 34149 Basovizza, Trieste, (Italy) [e]Labor Artis C.R. Diagnostica S.R.L., Via Celona, Palermo (Italy)

Hydrophobic treatment is one of the most important interventions usually carried out for the conservation of stone artefacts and monuments [1]. The study here reported aims to answer a general question about how two similar polymers can confer different protective performance. Two fluorinated-based formulates applied on samples of Cusa's stone impair a different water repellency and water vapour permeability. The observed protection action [2] is here explained on the basis of chemical-physic interactions. The distribution of the polymer in the pore network was investigated by Scanning Electron Microscopy and X-ray Microscopy [3]. The interactions between the stone substrate and the protective agents were investigated by solid state NMR spectroscopy. ss-NMR findings revealed no significant changes in the chemical neighbourhood of the observed nuclei of each protective once applied on stone surface and provided information about the mobility of polymer chains [4]. The variation of polymer chains mobility is an evidence of their different structural organization inside porous system and suggest the formation or not of a homogeneous surface film and along the pore walls that could justifies the observed water repellency or water vapor permeability because of a small accumulations of the material inside the pores of the stone. Results allowed us to explain the different macroscopic behaviour given by each protective to the stone substrate. This new methodological approach is fundamental for predicting and obtaining indirect information on protective treatments and represents an alternative approach to the traditional methods used up to now. The obtained results are of utmost importance for the fundamental research, but also for manufacturing companies aiming to developing new commercial products or upgrading existing ones.
Results will be presented and discussed.

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Oxidative stability and polyphenols role in red wine-enriched olive oil emulsions

Giuseppe Cinelli[1], *Francesca Cuomo*[1], *Andrea Ceglie*[1], *Francesco Lopez*[1]

[1] *Department of Agricultural, Environmental and Food Sciences (DiAAA) and Center for Colloid and Surface Science (CSGI), University of Molise, Via De Sanctis, I-86100 Campobasso, Italy.*

Vegetable oils are extensively used as food emulsions ingredients for their nutritional and sensory properties. Nevertheless, these matrices are prone to oxidation because they are composed mainly of unsaturated fatty acids. Red wine, due to its rich pool of phenolic compounds, is well recognized as a source of beneficial molecules with antioxidant activity. Wine drinking, however, should be done in moderation or is forbidden for some populations for ethnic or religious reasons. Thus, a suitable way to enjoy the advantages of red wine is to use its phenolic compound-rich extract (RWE).
In this study, the antioxidant activity of water-soluble RWE has assessed in water-in-oil (w/o) emulsions based on extra virgin olive oil. After the selection of the right emulsion composition, kinetics of oil oxidation were carried out in oil and emulsions in the presence of an increasing amount of RWE, whose presence was demonstrated to influence the oxidation rate. This behavior was confirmed by monitoring the oxidation process firstly by applying the classical method based on the determination of the peroxide value, then by considering the fluorescence response based on the accelerated test making use of 2,2′-azobis(2,4-dimethylvaleronitrile) (AMVN) and diphenyl1-pyrenylphosphine (DPPP) [1,2]. The comparison between the emulsion aspect confirmed that the extent of the oxidation process was inversely proportional to the RWE concentration. Moreover, by comparing the emulsion structures observed by optical microscopy, no differences in the size of the dispersed aqueous phase were detected with the increase of the RWE, which is an aspect that confirmed that the antioxidant activity was directly proportional to the RWE concentration and thus to the phenolic content present in the system.

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Rheological Characterization of Hydrogels of Alginate-Based Nanodispersion

Martina Cofelice[1], *Francesca Cuomo*[1], *Andrea Ceglie*[1], *Francesco Lopez*[1]

[1] *Department of Agricultural, Environmental and Food Sciences (DiAAA) and Center for Colloid and Surface Science (CSGI), University of Molise, Via De Sanctis, I-86100 Campobasso, Italy*

The interest in alginate-based systems is due to the wide potential of application of this macromolecule in several fields ranging from pharmaceutical, medical to coating and food industries.
Here, we present alginate-based hydrogels prepared through the in situ gelation method [1] driven by calcium cross-linking. The gelation process was applied on oil-in-water nanodispersions of lemongrass essential oil in alginate, stabilized by a non-ionic surfactant (Tween 80).
Hydrogels prepared at different concentrations of alginate (0.5-1%), essential oil (0, 0.1 and 0.5%) and calcium (4, 6, 8 and 10 mM) were characterized for their rheological behavior.
First, flow curves demonstrated that all the hydrogels shared pseudoplastic behavior. Then, oscillatory tests showed that the strength of the hydrogel network increased with the crosslinker increase and decreased at low polymer concentrations [2, 3].
Hydrogels were also characterized for their time-dependent behavior and resulted as thixotropic materials with a long time of structural restoration after breakage. Finally, creep-recovery experiments that were all fitted to the Burger model, showed that hydrogels with low alginate concentration were more deformable and that the deformation was reduced by the increase of oil content. On the other hand, the deformability decreased both with the alginate and the crosslinker concentration increase.
The outcomes of this study showed that the mechanical characteristics of the proposed hydrogels were mainly influenced by the concentration of alginate and the crosslinking agent.

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Chemical–physical and dynamical–mechanical characterization on Spartium junceum L. cellulosic fiber treated with softener agents

G. A. Corrente, F. Scarpelli, P. Caputo, C. Oliviero Rossi, A. Crispini, G. Chidichimo, A. Beneduci

Department of Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Cubo 15D, 87036 Arcavacata di Rende (CS), Italy

In the last decades there was an increasing world attention towards the maximum utilization of recyclable resources and to an eco-sustainable and environmentally friendly development. In the textile sector, there is still a strong interest on the development and production of chemical synthetic fibres based on non-renewable fossil-fuels [1,2]. However, the increasing production costs of petroleum-based materials, and the costs associated to their environmental impact, have heightened the need for using renewable natural fibres. Cotton and linen are the most known and used natural fibers in the textile sector, but their production requires large land usage at the expenses of other food crops. Since the food demand is increasing, it is necessary to search for sustainable food productions that do not heavily impact on the ecosystems [3]. A valid alternative is to extract fibers from rapidly and spontaneously growing shrubs such as Spanish broom (Spartium junceum L., SJ), which is endemically distributed almost in all over the world. We developed an automated production process based on an alkaline pre-treatment of the shrub in a 5% (w/w) of sodium hydroxide water solution, followed by the separation of the cellulose fiber by means of specific brushes that mechanically harvest the long fibers [4]. The S.J. long cellulose fiber was chemically treated with different softening agents with the aim to improve its textile applicability. The effects of the softening agents on the fiber was evaluated quantitatively, by macroscopic measurements of the wettability, viscoelasticity, and thermal properties. Moreover, the effects of the softening treatments on the microscopic structure of the fiber and on its properties at a molecular level, were studied by optical and scanning electron microscope and X-ray diffraction, respectively [5]. The characteristics of the extracted fiber are very important to obtain high quality product fabrics.

Figure 1: Representative samples of the raw (a) and treated cellulose fiber with the chemical softener (b). Prototypes of dresses for women, a trench coat and a jumpsuit, with broom and linen fibers (c).

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Magnetic nanoparticles for oxidative enzyme immobilization: comparison of different synthetic routes and substrate reactivity

Jessica Costa, Andrea Atrei, Rebecca Pogni

Department of Biotechnology, Chemistry and Pharmacy, University of Siena, Via Aldo Moro 2, 53100 Siena, Italy

Enzymes are very efficient biocatalysts that catalyze numerous biochemical and chemical reactions under mild reaction conditions such as ambient temperature, physiological pH, and aqueous environment, etc. They found many industrial applications for their important advantages compared to the chemical processes. Nevertheless, their use at industrial level is seriously hampered by low operational stability and marginal lifetime. Among the various modification approaches, the enzyme immobilization is a preferred strategy to improve the enzyme catalytic stability for different applied purposes [1]. Nanotechnology has been applied to enzymatic immobilization, especially the use of magnetic nanoparticles (MNPs) has gained significant attention due to their magnetic properties, low toxicity and biocompatibility [2]. Nanoparticles present large specific surface area, easy separation under external magnetic fields, and high mass transference, suitable characteristics as support in catalytic systems. MNPs of different types and sizes are now being synthesized via several physical and chemical methods. The co-precipitation technique is probably the simplest and most efficient chemical pathway to obtain magnetic particles. A wide variety of factors can be adjusted in the synthesis of iron magnetic nanoparticles to control the size, magnetic characteristics or surface properties. MNPs display their greatest performance at typical sizes ranges from 10 to 20 nm. Here the MNPs were synthesized following two different methods for the immobilization of the oxidative enzyme *T. versicolor* laccase. The MNPs obtained with the two synthetic procedures showed a different degree of dispersion. The enzyme was immobilized on the MNPs obtained with the two synthetic methods and a different enzyme reactivity was detected changing substrates. A physico-chemical characterization of the supported MNPs has been performed highlighting the different aspects influencing the use of MNPs for the immobilization of oxidative enzymes compared to other classes of enzymes [3].

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Study of ITO nanoparticles by solid state NMR spectroscopy

Elisa Della Latta,[a] Marco Geppi,[a,b] Ananthakrishnan Mohan, [a] Federica Daus,[a] Francesco Pineider,[a] Silvia Borsacchi,[c,b] Francesca Martini[a,b]

[a]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56124 Pisa, Italy; [b]Centro per l'Integrazione della Strumentazione Scientifica dell'Università di Pisa (CISUP), 56126 Pisa, Italy; [c]Istituto di Chimica dei Composti Organo Metallici, Consiglio Nazionale delle Ricerche (CNR-ICCOM), 56124 Pisa, Italy

Recently nanoscience and nanotechnology have sparked a lot of interest in many fields of science and engineering. In the field of plasmonics, noble metal nanoparticles (NPs) exhibit optical properties that differ significantly from those of the bulk. Indeed, they show a strong absorption band in the UV-Vis region due to coherent oscillation of conduction electrons, driven by the electric field of light. This phenomenon is called "Localized Surface Plasmon Resonance" (LSPR) and the position of the resonant peak depends on the size of the metal nanoparticle [1]. Plasmonic NPs are currently object of considerable interest thanks to their wide range of potential applications in the fields of nano-optics, chemical and biological sensing, spectroscopy and molecular imaging. Lately, doped semiconductors, including tin-doped indium oxide (ITO), have been proposed as new cheaper nanomaterials with plasmonic properties. Unlike noble metal NPs, ITO is a near-infrared plasmonic system and the resonant peak can be easily tuned by changing the dopant concentration [2]. Due to its properties, it has been employed in electrochromic windows [3], solar cells, flat-panel displays, sensors and architectural glasses [4]. Investigating their structural features at an atomic/molecular level can improve our understanding of the final properties of these materials. Recently [5] ^{119}Sn solid state NMR (SSNMR) has proved to be of particular interest for the study of ITO NPs. In this work we investigated the structural properties of ITO nanoparticles, stabilized with oleylamine, with different doping concentration by using high resolution SSNMR. ^{119}Sn DE/MAS (Direct Excitation/Magic Angle Spinning) measurement were performed to investigate the effect of doping on the structure and electronic properties. Moreover, ^{13}C and ^{1}H MAS experiments were carried out in order to get insights into the arrangement and dynamics of the stabilizer around the nanoparticles.

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Photocatalytic Antimicrobial Inactivation By TiO_2-Based Nanostructured Materials

Ilaria De Pasquale[a], Massimo Dell'Edera[a,b], Chiara Lo Porto[a], Elisabetta Roberto[b], Angela Agostiano[a,b], M. Lucia Curri[a,b] and Roberto Comparelli[a]

[a]CNR-IPCF, Istituto per i Processi Chimico-Fisici, S.S. Bari, c/o Dip. Chimica Via Orabona 4, 70126 Bari, Italy; [b]Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Via Orabona 4, 70126 Bari.

Photocatalytic TiO_2 nanoparticles (NPs) are receiving a great deal of attention owing to their potential applications in environmental remediation. In particular, TiO_2 based nanomaterials are among the most studied materials in the field of photocatalytic antimicrobial applications, due to their ability in disinfection/inactivation of harmful pathogens (bacteria, fungi, and virus) [1, 2]. Indeed, TiO_2 based NPs can be effectively applied in water treatment (e.g. anti-biofouling membranes), disinfection of building materials, biomaterials and food packaging and processing materials, air remediation, self-cleaning applications, cultural heritage protection and bactericidal surface. The antimicrobial activity of this class of materials can be ascribed to their ability in photogenerate, under band-gap irradiation, reactive oxygen species (ROS) that degrade organic matter forming living microorganism. In addition, the extension of light absorption ability of TiO_2 based photocatalysts to the visible region of the electromagnetic spectrum of nano-TiO_2) can be achieved, for instance, combining TiO_2 with NPs metal (such as Ag, Cu, Mn, Al, etc.), thus further increasing the potential of the antimicrobial effect of this class of nanostructures [3]. On these bases, here, TiO_2 NPs and TiO_2 NPs/Ag hybrid nanostructures were synthesized and their antimicrobial activity was tested in aqueous medium under different experimental conditions, in order to single out the photocatalytic effect on the microbial inhibition process [4]. The inhibition activity was assessed against different microorganisms, to evaluate the possible effect of their structural differences (*Escherichia coli*, *Enterococcus hirae*, *Bacillus cereus* and *Candida albicans*). In all the experiments TiO_2 P25 (Evonik) was used as benchmark catalyst. The preliminary results (**Figure 1**) highlighted an antimicrobial activity of TiO_2 NPs/Ag higher than that presented by TiO_2 NPs, with a 100% inhibition, comparable to that accomplished with commercial TiO_2 P25 reference.

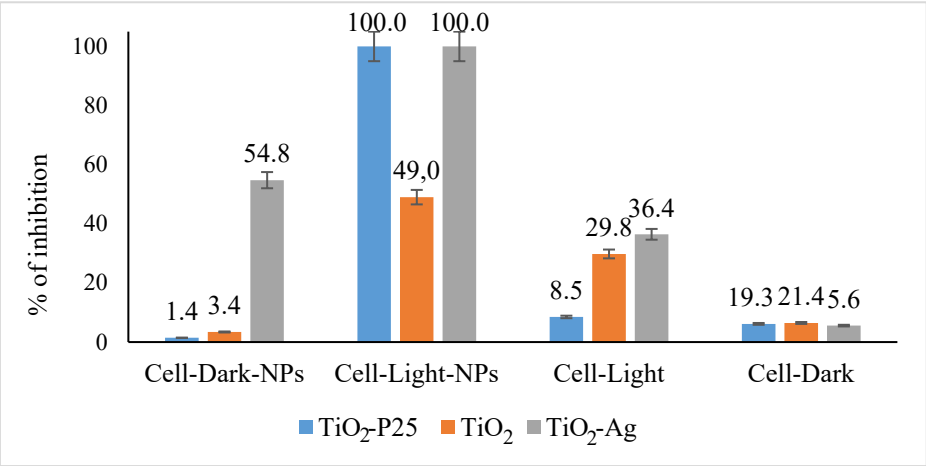

Figure 1- Results of the inhibition tests performed on Gram-negative bacteria, *Escherichia coli*, assisted by TiO_2 (in orange) and TiO_2 NPs/Ag hybrid (in grey) and TiO_2 P25 standard (in blue) as reference, under different experimental conditions (dark, light and presence/absence of NPs).

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PROBING THE ULTRAFAST DYNAMICS IN BIOLOGICAL SYSTEMS: THE ROLE OF THE HYDROGEN BONDS

Elisa Fresch[a], *E. Meneghin*[a], *A. Agostini*[a,b] , *H. Paulsen*[b], *D. Carbonera*[a], *E. Collini*[a]

[a] *Department of Chemical Sciences, University of Padova, Padua, Italy;* [b] *Institute of Molecular Physiology, Johannes Gutenberg-University, Mainz, Germany*

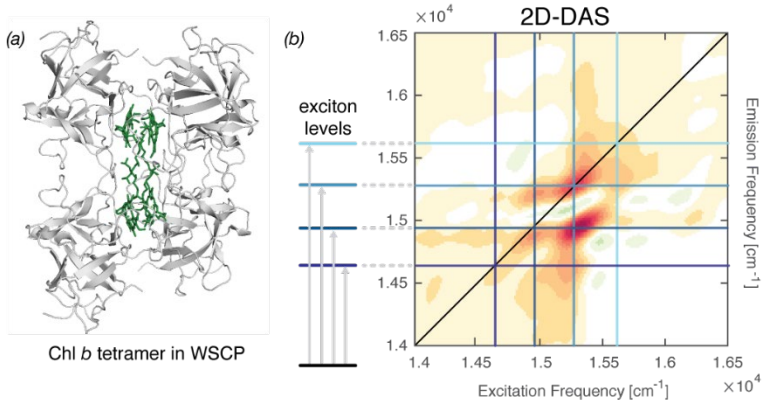

Figure 1. (a) Crystallographic structure of WSCP where the Chl tetramer is recognizable. (b) The 2D-DAS of Chlb-WSCP obtained from the global fitting procedure, where the four excitonic energy levels are highlighted.

It is well known that the establishment of specific and directional interactions could affect the functionality and the dynamics of biological and artificial complex systems. Particular attention has recently been focused on the role that hydrogen bonds (H-bonds) play in changing the dynamical properties of electronic excited states.[1,2] In this work, we investigated the ultrafast relaxation dynamics of a biological pigment-protein complex, the Water-Soluble Chlorophyll-binding Protein (WSCP), to probe and verify how the presence of H-bonds could affect the photophysics of the excited state. 2D-Electronic Spectroscopy was applied for this purpose since it allows to follow the ultrafast dynamics of complex systems, providing information on the temporal evolution of both coherent and non-coherent processes with a time resolution in the order of femtoseconds.

We found that the directional nature of H-bonds has important implications for the electronic properties of the WSCP: the electronic properties of the pigments, namely the transition dipole moment and then also the electronic coupling and the excitonic energy gaps are tuned by the presence of specific and directional interactions between the protein backbone and the formyl group on the Chl *b* moiety.[3] These findings suggest that the design of H-bonded structures implies the possibility of tuning the photophysics and the transport properties of complex systems by engineering specific interactions with the surroundings.

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Hierarchically self-assembled induced by hydrophilic coating: the case of CeO_2 nanoparticles.

Noemi Gallucci [a,b], Giuseppe Vitiello [b,c], Rocco Di Girolamo [a], Oreste Tarallo [a], Alessandro Vergara [a], Paola Imbimbo [a], Daria Maria Monti [a], Alessandra del Giudice [b,d], Luciano Galantini [b,d], Irene Russo Krauss [a,b], Luigi Paduano [a,b]

[a] Department of Chemical Sciences, University Federico II, Naples, Italy; [b]CSGI-Center for Colloid and Surface Science, Sesto Fiorentino, Italy; [c] Department of Chemical, Materials and Production Engineering, University Federico II, Naples, Italy; [d] Department of Chemistry, University La Sapieza, Rome, Italy.

Nanoparticles are used in various fields for their specific properties, which can be further implemented if induced to form superlattices [1-2]. In this respect, we recently synthesized cerium oxide nanoparticles (CeO_2-NPs) by thermal decomposition of $Ce(NO_3)_3 \cdot 6H_2O$, using as capping agents either octylamine or oleylamine, to evaluate the effect of alkyl chain length and temperature on NP properties [3]. The NPs thus obtained were extensively characterized by means of several techniques, such as Wide-angle X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS), UV-vis, Fluorescence, Raman, and FTIR spectroscopy allowing us to define the role of the synthesis conditions in affecting the shape and size of NPs as well as their optical properties. In fact, octylamine increases the concentration of Ce^{3+} resulting in a wide absorption throughout the whole UV-vis region. On the other hand, oleylamine increases the relative quantum yields of CeO_2-NPs. Furthermore, among the synthesized CeO_2-NPs those with the smallest size and the best separation in solution were functionalized by means of interaction between the alkyl chains of capping agents (oleylamine) and those of another amphiphilic molecule (either sodium oleate or oleic acid). The formation of ordered aggregate (due to the oleylamine-oleic acid interaction; such as Frank-Kasper phases) or disordered aggregate (due to the oleylamine-sodium oleate interaction) modifies the physico-chemical properties of CeO_2-NPs, above all the optical properties, which are different from those of single CeO_2-NPs. Finally, MTT assays on eukaryotic cells were carried out with the aim to assess the biocompatibility and the antioxidant activity of selected samples.

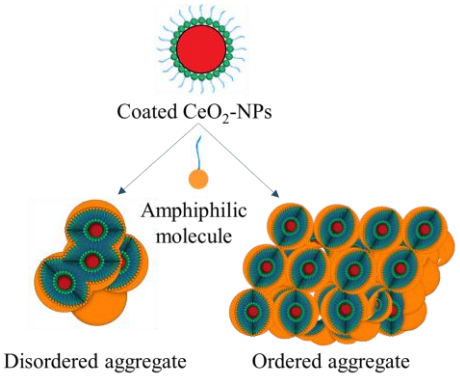

Figure 1. *Schematic representation of the functionalization process.*

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Structural properties of the F4_MIL-140A(Ce) MOF by solid-state NMR spectroscopy

Andrea Giovanelli,[a] Francesca Martini,[a,b,c] Lucia Calucci,[c,b] Marco Taddei,[a,b] Marco Geppi[a,b,c]

[a]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56124 Pisa, Italy; [b]Centro per l'Integrazione della Strumentazione Scientifica dell'Università di Pisa (CISUP), 56126 Pisa, Italy; [c]Istituto di Chimica dei Composti Organo Metallici, Consiglio Nazionale delle Ricerche (CNR-ICCOM), 56124 Pisa, Italy

Metal-Organic Frameworks (MOFs) are a class of crystalline compounds whose scaffolding derives from metal clusters or ions that are interconnected by organic linkers. The high number of possible combinations of metals and ligands leads to high tunability of macroscopic properties and thus it is possible to employ MOFs in many fields of applications, including gas storage [1], gas separation [2], catalysis [3] and others [4,5]. During the design and development of a new MOF, it is extremely important to completely understand every macroscopic property of the compound and to relate it to its microscopic origin.

Many techniques can be exploited and combined to characterize the structural and dynamic molecular properties of a MOF. Among them, Solid State Nuclear Magnetic Resonance (SSNMR) spectroscopy is certainly one of the most important because it can shed light on many aspects of the compound at a molecular level, such as 3D structure [6], porosity [7], local dynamics [8], and host-guest interactions [9].

In this work, ^{1}H, ^{13}C, and ^{19}F SSNMR spectroscopy has been employed to gain an in-depth knowledge of a MOF belonging to the MIL class, precisely F4_MIL-140A(Ce), in which chain-like inorganic building units of Cerium^{IV} are interconnected by tetrafluoroterephtalates. This MOF is extremely promising for possible applications, in particular as a sorbent for gas separation, because of its water-based synthesis and its step-shaped CO_2 adsorption isotherm [10].

High-resolution SSNMR techniques and 2D correlation spectra have been used to obtain, also by comparison with powder X-ray diffraction results, a detailed characterization of the framework structure both in the presence and after removal of crystallization water, highlighting the presence of different molecular environments with different symmetry. Particular attention has been put into the investigation of dynamic processes involving the fluorinated aromatic rings through the variable-temperature analysis of ^{19}F spin-lattice relaxation times and ^{13}C chemical shift anisotropy.

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Synthesis and characterization of functional geopolymeric-based materials for building sector application

Fausta Giacobello [a], *Ileana Ielo* [a], *Francesco Parisi* [b], *Giuseppe Nania* [b], *Drommi Dario* [c], *Giuseppe Sabatino* [b], *Maria Rosaria Plutino* [a]

[a] *Institute for the Study of Nanostructured Materials, ISMN – CNR, Palermo, c/o Dep. ChiBioFarAm, Univ. Messina, Viale F. Stagno d'Alcontres 31, Vill. S. Agata, 98166 Messina, Italy* [b] *Department of Mathematical and Computer Sciences, Physical Sciences and Earth Sciences, and* [b]*Department ChiBioFarAm, Univ. Messina, University of Messina, Viale F. Stagno d'Alcontres 31, Vill. S. Agata, 98166 Messina, Italy.*

In the last decades, new synthetic materials with inorganic and organic nature were developed with the aim of promoting their application as protective coatings and/or structural consolidants for several substrates in construction sector. In this context, the scientific community focused the attention on geopolymers and new hybrid compounds deriving from these ones, in order to study and design innovative materials with better chemical resistance, durability and mechanical characteristics.
Geopolymers are one of the potential substitutes for cement-based composites. These are ceramic-like inorganic polymers obtained from a reactive powder, source of silicon and aluminium, such as clays, fly ashes or waste materials and an activating alkaline solution, commonly sodium or potassium hydroxide [1]. These materials are featured by scarce rheological properties due to their low viscosity, which make them almost inapplicable in restoration works mostly of vertical buildings. To overcome this problem, scientists has recently tried to improve the chemical, physical and mechanical properties of these compounds by formulating hybrid organic - inorganic systems. These new binders, consisting of geopolymers with an organic component, are synthesized by means of a cross-link reaction that occurs between the inorganic phase and the organic one, such as polysiloxane oligomers, alcoxysilane agents or epoxy resin precursors [2]. The functionalization of the alkali - activated material with the organic component improves the performance of the system, as it allows an increase in the viscosity of the mixture, making the hybrid material more versatile in architectural and renovation of buildings [3]. The synthesis process of these hybrid materials takes place via the sol – gel method, which is an eco-friendly approach to functionalize geopolymers, without high temperature treatments, in accordance with the principles of circular economy and green chemistry [4]. The present work concerns the modification of the geopolymer at the chemical and nanostructural level, through the condensation process in alkaline conditions, by using alkoxysilane and polysiloxane agents for the implementation of their properties. Their chemical properties, together with the precursor ones, were studied by using X-ray fluorescence and diffraction investigations in order to correlate geopolymers structure with their properties.

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Tailoring the size, shape and phase of colloidal plasmonic copper sulphide nanocrystals

M. Giancaspro,[a] T. Sibillano,[b] F. Panzarea,[a] C. Giannini,[b] S. Schmitzer,[a] F. Vischio,[ac] N. Depalo,[c] A. Agostiano,[ac] M. L. Curri,[ac] M. Striccoli,[c] E. Fanizza [ac]

[a] Chemistry Department, Università degli Studi di Bari, Via Orabona 4, 70126 Bari, Italy;[b] CNR-Istituto di Cristallografia (CNR-IC), Via Amendola, 122/O, 70126 Bari, Italy;[c] CNR-Istituto per i Processi chimico Fisici (CNR-IPCF), SS Bari, Via Orabona 4, 70126 Bari, Italy

Self-doped copper sulphide $Cu_{2-x}S$ nanocrystals (NCs) are p-type semiconductors with fascinating near infrared (NIR) plasmonic properties that show to be very beneficial in a wide variety of applications such as catalysis, energy conversion, sensing and biomedicine.[1,2] Due to their stoichiometry-, size- and shape- dependent properties, the NCs design is essential for producing high performances devices. Even though progress in controlling geometry and optical properties has been made so far in $Cu_{2-x}S$ NCs synthesis by hot injection, unexpected sizes and shapes and broad polydispersity still represent critical problems, that lead to unpredictable optical responses and contribute significantly to the broadening of spectroscopic features. This work aims to address such limitations giving an insight into the influence of reactants on $Cu_{2-x}S$ NCs size, shape and phase modulation.

Various conventional copper precursors (i.e. CuCl, $CuCl_2$, $Cu(AcAc)_2$, $Cu(AcO)_2$), sulphur reactants (i.e. S_8, tert-dodecanthiol (tDT) or dibuthyldisulfide (DBDS)) and coordinating solvents (oleic acid, OA and oleylamine, Olam) have been used to prepare $Cu_{2-x}S$ NCs by hot injection methods. The reactivity of copper salt precursors, considered with respect to metal ion valence and type of counterions, and the strength of ligand bindings to NC surface, have been evaluated through the Hard Soft Acid Base (HSAB) principles. A systematic morphological, structural and spectroscopic analysis of $Cu_{2-x}S$ NCs samples have been carried out.

The CuCl> $CuCl_2$> $Cu(AcO)_2$> $Cu(AcAc)_2$ order of reactivity directly affect the rate of monomer release controlling the size and shape monodispersity. While the type of counterions, balanced by the ligand composition, has been proven to define the final NC shape when S_8 is used as sulfur precursor, in the case of alkanethiol, the formation of hexagonal monodispersed thin NPLs is templated by hexagonal discotic micellar structures of chloride Cu-tDT liquid crystalline phase. The intrinsic poor reactivity of organosulphur, injected *in situ* provides the djurlite $Cu_{1.94}S$ whereas S_8, decomposed *ex situ* in coordinating reducing solvent, has led to digenite $Cu_{1.8}S$ NCs. Overall, this work has effectively contributed to the fundamental understanding of the complex mechanism responsible for the formation of $Cu_{2-x}S$ NCs, providing a valuable toolbox, based on precursors and reactants and chemical considerations, to achieve NCs with controlled structural and morphological characteristics and well defined plasmonic response, thus suited for future technological applications.

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Sensitivity enhancement and quantitative aspects of ^{29}Si solid state NMR spectra

Giulio Giannessi,[a] Francesca Martini,[a,b] Silvia Borsacchi,[b,c] Roberto Francischello,[a] Marco Geppi[a,b]

[a]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56124 Pisa, Italy; [b]Centro per l'Integrazione della Strumentazione Scientifica dell'Università di Pisa (CISUP), 56126 Pisa, Italy; [c]Istituto di Chimica dei Composti Organo Metallici, Consiglio Nazionale delle Ricerche (CNR-ICCOM), 56124 Pisa, Italy

^{29}Si solid state NMR spectroscopy (SSNMR) has proven to be a valuable tool for the characterization of silicon-based materials. ^{29}Si SSNMR techniques have indeed been applied to the study of a wide variety of systems, such as silica and silicate surfaces [1] and cements [2]. The utility of ^{29}Si SSNMR arises from the extreme sensitivity of ^{29}Si chemical shift to the local chemical environment, and in particular to the number of bridging oxygen and OX groups (X = H, R) bonded to the observed ^{29}Si nucleus; therefore, signals of M ($R_3SiO_{0.5}$), D ($R_2Si(O_{0.5})_2$), T ($RSi(O_{0.5})_3$), and Q ($Si(O_{0.5})_4$) silicon species fall in different regions of the SSNMR spectrum. Unfortunately, ^{29}Si NMR presents some inherent downsides, mainly related to the scarce isotopic abundance (4.67%) of ^{29}Si nuclei and to their long spin-lattice relaxation times T_1. These features can extremely dilate (from several hours to days) the experimental time for acquisition of quantitative direct excitation (DE) spectra and, for this reason, non-quantitative and less time-consuming approaches are often preferred. ^{1}H-^{29}Si cross polarization (CP) is among the most employed techniques for recording ^{29}Si SSNMR spectra with enhanced sensitivity at the expense of quantitative information.

In this work, different approaches based on several DE and CP techniques for recording ^{29}Si SSNMR spectra were discussed and compared in terms of sensitivity and quantitative aspects, in order to identify the most efficient experimental approach for the desired information. In some cases, these experiments were coupled with modern noise reduction techniques [3]. In particular, the different methods were applied on a sample of silica functionalized with 3-(trimethoxysilyl)propyl methacrylate (TSPM) [1], used as filler in polymeric materials. In this kind of systems the observation and quantification of T silicon species is fundamental to assess the efficiency of the functionalization reaction and to understand the properties of the final composite materials. Beside "standard" CP experiments, recently developed Multiple-Cross Polarization (MultiCP) techniques [4], combining the enhanced sensitivity of CP with the possibility of retaining quantitative information, were also tested. Notably, in the last few years, MultiCP experiments have been successfully employed to record quantitative ^{13}C spectra of organic materials with good signal-to-noise ratios, and their application to ^{29}Si is currently being explored [5,6].

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The role of the functional group on co-condensed mesoporous silica nanoparticles pore structure

Alessandro Gottuso[a], *Francesco Armetta*[a], *Francesco Parrino*[b], *Maria Luisa Saladino*[a]

[a] *Dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche, STEBICEF and INSTM UdR, Palermo, Università di Palermo, Viale delle Scienze Ed. 17, 90128 Palermo, Italy*

[b] *Dipartimento di Ingegneria Industriale (DII), Università degli Studi di Trento, Via Sommarive 9, 38123 Trento, Italy*

In this work, three different functionalized mesoporous silica nanoparticles (MSNs) were synthesized through the co-condensation synthesis in oil/water emulsion. [**1**,**2**] Hexadecyltrimethoxysilane, triethoxy-3-(2-imidazolin-1-yl)propylsilane and (3-mercaptopropyl)triethoxysilane were used as organ-substituted silica precursors with variable molar ratio with respect to tetraethoxysilane (TEOS, 1:4, 1:9, 1:19). The occurred functionalization was investigated by ^{29}Si {1H} CP-MAS-NMR, ATR-FTIR and FT-Raman spectroscopy. The role of the different pendant groups on the mesostructured pore organization of the obtained nanoparticles was evaluated by means of Transmission Electron Microscopy (TEM) and N_2 sorption measurements. The used method seems to be well suited for the proposed pendant groups since the results show an effective surface modification for all the three functional groups, although for each of them some different structural modifications in pore morphology are observed due to the different interactions between silica precursors and the components of the emulsion.

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Infiltration of electrospun Gd-doped ceria nanofibers by a (Ba, Sr, Cu, Fe) solution: an experimental study

D. Grilli [a], *A. Cingolani* [a], *C. Sanna* [a], *S. Massardo* [a], *M.M. Carnasciali* [a,b], *M. Pani* [a,c], *P. Costamagna* [a], *C. Artini* [a,d]

[a] *DCCI, Department of Chemistry and Industrial Chemistry, University of Genova, 16146 Genova, Italy ;* [b] *INSTM, Genova Research Unit, 16146 Genova, Italy;* [c] *CNR-SPIN Genova, 16152 Genova, Italy;* [d] *CNR-ICMATE, Genova Research Unit, 16149 Genova, Italy.*

Rare earth (RE)-doped ceria (RE ≡ Gd, Sm) is characterized by high values of ionic conductivity between 673 and 973 K, which make it a widely studied material to be used as an electrolyte in solid state cells working in the intermediate temperature range (IT-SOCs) [1]. Thanks to this property, it is also often mixed to the electrode material in order to enhance the ionic conductivity of the latter, and to make it a good mixed ionic-electronic conductor (MIEC). The relatively low operating temperature on one hand slows down the degradation process of the cell, but on the other hand it also lowers the cell performance, negatively affecting the electrode kinetics. For this reason, it is necessary to improve the electrode architecture, for instance by maximizing its surface area, in order to extend the three-phase boundary (TPB) in the interior of the electrode bulk.

Within this framework, electrospinning acts as a powerful tool for the production of 1D materials, such as nanofibers (Figure 1) of composite electrodes, like the ones formed of a mixture of a perovskite-based electronic conductor (e.g. La, Sr, Cu, Fe oxides) and RE-doped ceria [2].

Aim of this project is to study the infiltration of $(Ce_{1-x}Gd_x)O_{2-x/2}$ (x = 0.10, 0.15 and 0.20) electrospun nanofibers by a water-based solution containing Ba, Sr, Cu and Fe.

Following this procedure, it is possible to enhance the ionic conductivity in the whole electrode thickness, and thanks to the perovskite-based nanoparticle $Ba_{0.5}Sr_{0.5}Cu_{0.4}Fe_{0.6}O_{3-x}$ (BSCuF) dispersed in the GDC nanofibers network, it is possible to increase the TPB sites extending the reaction in the whole electrode. This feature is expected to significantly improve the catalytic performance.

The effect of the infiltration process depends on the quality of the network, such as the fibers average radius, surface and porosity.

In this work the method of infiltration by deposition is studied, focusing on the different effect obtained by depositing on the electrode a single drop of BSCuF solution or more drops in subsequent steps.

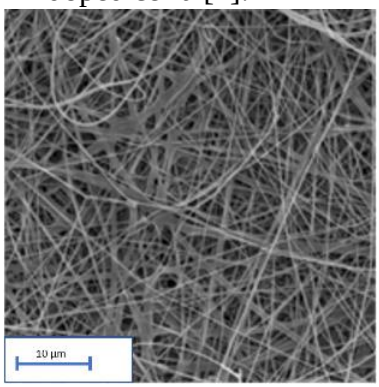

Figure 1: GDC10 nanofibers, SEM SE.

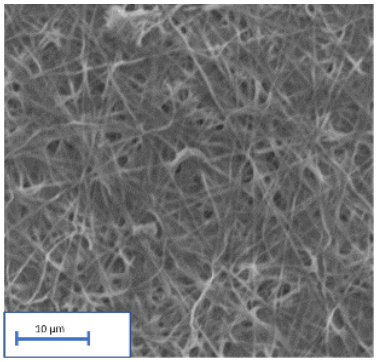

Figure 2: GDC10 nanofibers infiltrated by 10 µL of BSCuF solution, SEM SE.

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The effect of nonionic surfactants on polymer film dewetting and artificial soil removal from artistic surfaces

Teresa Guaragnone[a], Michele Baglioni, Rosangela Mastrangelo, Felipe Hidetomo Sekine, Taku Ogura, Piero Baglioni

[a] Department of Chemistry and CSGI, University of Florence, via della Lastruccia, 3, 50019 Sesto Fiorentino, Florence, Italy; [b] Research Institute for Science & Technology, Tokyo University of Science, 2641, Yamazaki, Noda-shi, Chiba 278-8510, Japan; [c] NIKKOL GROUP Nikko Chemicals Co., Ltd., 1-4-8, Nihonbashi-Bakurocho, Chuo-ku, 103-0002 Tokyo, Japan

The removal of unwanted layers –natural or synthetic– represents one of the most common interventions on artistic surfaces [1]. In these cases, the use of nanostructured fluids (NSFs) like micellar solutions and microemulsions provides significant improvements over the use of traditional cleaning techniques, i.e., the use of non-confined organic solvents, water, or aqueous solutions. Cleaning effectiveness of NSFs in applicative context is strictly connected to the effects of each component of the fluid; for this reason, understanding the role and properties of surfactants in NSFs formulations is mandatory. Moreover, the search for innovative and highly performing amphiphiles is one of the main goals in the field of Cultural Heritage conservation.
This work reports on the use, for the first time, of methoxy-pentadeca(oxyethylene) dodecanoate (MPD) surfactant [2] in two different NSFs. Its behavior is compared to a conventional nonionic amphiphile used in conservation, pentadeca(oxyethylene) dodecyl ether (PDE), for the removal of ParaloidTM B72 and artificial soil from flat surfaces. The mechanism through which NSFs interact with polymeric coatings or soiled surfaces was investigated by confocal laser scanning microscopy (CLSM), fluorescence correlation spectroscopy (FCS), photographic observation, small-angle X-ray scattering (SAXS), contact angle and surface tension measurements. The results highlighted the superior MPD's performance, both in inducing polymer removal and in detaching the soil from coated surfaces. At the microscale, the removal involves dewetting-like processes, where the polymer or the soil oily phase detaches from the surface and coalesces into separated droplets. The observed behavior is consistent with the different surface tensions and the different adsorption mechanisms of MPD with respect to ordinary nonionic surfactants, likely due to the methyl capping of the polar head chain and to the presence of the ester group between the hydrophilic and hydrophobic parts of the MPD surfactant molecule. Overall, this work underlines how a tiny change in the surfactant architecture can lead to important differences in the cleaning capacity.

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Design, development and characterization of functional sol-gel based geopolymer coating for conservation and restoration of cultural heritage

Ielo I[a], Giacobello F[a], Galletta M[b], Franzone M[c], Nania G[c], Drommi D[b], Sabatino G[b], Plutino MR[a]

[a]*Institute for the Study of Nanostructured Materials, ISMN–CNR, Palermo, c/o Department of ChiBioFarAm, University of Messina, Viale F. Stagno d'Alcontres 31, Vill. S. Agata, 98166 Messina Italy;* [b]*Department of Chemical, Biological, Pharmaceutical and Analytical Sciences (ChiBioFarAm), and* [c]*Department of Mathematics and Informatics, Physic and Earth Sciences (MIFT), University of Messina, Viale F. Stagno d'Alcontres 31, Vill. S. Agata, 98166 Messina, Italy.*

Geopolymers are inorganic materials analogous to ceramics, which are mainly composed by aluminates and silicates [1]. The geopolymerization process occurs treating any inorganic source of silica and alumina with an alkaline solution of sodium or potassium hydroxide. Natural clays are commonly used in the synthesis of geopolymers, this work involves chemical modification of the geopolymer, as a result of the design and development of hybrid alcoxysilane-based sol-gel coatings, used to improve properties such as mechanical and thermal resistance, water resistance, water repellency, chemical inertness and porosity of the material for potential application in the restoration and conservation of cultural heritage [2]. The synthesis of functionalized geopolymers consists in the pre-treatment of the geopolymer mixture with the alkoxysilane sol-gel formulation and a siloxane cross-linker [3]. The selected alkoxysilanes have aromatic hydrocarbon groups or long-chain linear or branched aliphatic hydrocarbons [4]. The corrosion resistance and hydrophobicity of these geopolymeric monoliths are tested by immersion and wettability tests; microbial growth tests were also conducted to verify the antibacterial and antifouling activity. Other chemical-physical characterizations were performed to verify the improved surface properties in comparison to those of the geopolymeric precursors.

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Solid-State NMR study of a multiple-cation lead mixed-halide perovskite with high efficiency

Noemi Landi [a], Elena Maurina [a], Elisa Carignani [b], Silvia Borsacchi [b,c], Lucia Calucci [b,c], Daniela Marongiu [d], Michele Saba [d], Marco Geppi [a,b,c]

[a] Department of Chemistry and Industrial Chemistry, University of Pisa, via G. Moruzzi 13, 56124 Pisa, Italy; [b] Institute for the Chemistry of OrganoMetallic Compounds, Italian National Council for Research, CNR/ICCOM, via G. Moruzzi 1, 56124 Pisa, Italy; [c] Center for Instrument Sharing, University of Pisa (CISUP), 56126 Pisa, Italy; [d] Department of Physics, University of Cagliari, S.P. Monserrato-Sestu Km. 0700, Monserrato, 09042 CA, Italy.

Hybrid organic-inorganic metal-halide perovskites have emerged as highly interesting materials for various applications, such as thin-film photovoltaics or light-emitting devices, due to their outstanding optoelectronics properties. A main advantage of these materials is their tunability. Their macroscopic properties are intrinsically related to their microscopic features (*i.e.* atomic and molecular organization and dynamics), so mixtures of different cations and anions can be used to tune the optoelectronic properties and to enhance efficiencies and stabilities.
Their promising properties have brought about an increased effort in the research of these materials. Starting from methylammonium lead iodide ($MAPbI_3$), the archetypical hybrid halide perovskite material, several variations to the hybrid perovskite structure have been tested. In particular, the use of mixed-ion structures, in which the compositional complexity is increased by introducing dopants into the perovskite structure, has resulted in a remarkable improvement in perovskite solar cell performance. Thus, since their first use as sensitizers for solar cells in 2009 [1], perovskite solar cells have developed rapidly, achieving high power conversion efficiencies (well above 20%) and improved stability. Some of the latest top efficiencies have been reached by multiple-cation lead mixed-halide perovskites $(Cs,FA,MA)Pb(I,Br)_3$ [2][3][4].
However, the role of the dopants and additives in the high performance of the perovskite solar cells has not been fully understood yet, and its transferability to other perovskites is not straightforward.
For this reason, it is important to be able to gain atomic-level understanding of these materials.
Solid-State NMR (SSNMR) spectroscopy is strongly sensitive to the local chemical environment, and as such, it proved to be a perfectly suited technique to investigate mixed perovskites.
In this study, we focused on the perovskite with formula $Cs_{0.05}FA_{0.81}MA_{0.14}PbI_{2.55}Br_{0.45}$ because of its high performance. We investigated it by means of SSNMR for the first time, with $MAPbI_3$ being used as a reference compound. ^{207}Pb, ^{13}C and ^{1}H high-resolution SSNMR experiments allowed us to characterize the structure and composition of the samples, highlighting phase homogeneity and/or segregation, and to investigate ion dynamics by exploiting both spectral and relaxation properties.

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Revealing crystallization water in emissive and non – emissive Cs_4PbBr_6

Federico Locardi[a,c], Alberto Martinelli[b], Aniruddha Ray[a,c], Francesco Bisio[b], Stefano Toso[c], Emanuela Sartori[a,c], Ahmed Abdelhady[c], Liberato Manna[c], Maurizio Ferretti[a]

[a]Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy; [b]CNR-SPIN, corso F.M. Perrone 24, 16152 Genova, Italy; [c]Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

In the last years, the research on cesium lead halides has grown exponentially due to the peculiar optoelectronic properties shown by many materials within the Cs-Pb-X (X = Cl, Br, I) ternary system [1]. The crystal structure of these materials, whose general formula is Cs_nPbX_{2+n}, can be described as a cuboidal subnetwork of Cs^+ cations hosting $[PbX_6]^{4-}$ octahedra with a different degree of connectivity, that determines their optoelectronic properties. While the optical properties of higher-dimensionality structures (*e.g.* $CsPbBr_3$) are now well-known, the case of zero-dimensional structure, and specifically that of Cs_4PbBr_6, is still debated [2-3].

We synthesized emissive and non-emissive Cs_4PbBr_6 powders that we analyzed by X-ray Powder Diffraction (XRPD) and Pair Distribution Function (PDF) at the ID22 in the European Synchrotron Radiation Facility (ESRF). The results of our structural analysis led us to conclude that a mismatch between unit cell parameters and volumes between the emissive and non – emissive Cs_4PbBr_6 occurs. One plausible hypothesis is the inclusion of water molecules, that could be easily captured by such a highly ionic crystal during its growth. To prove our hypothesis, we performed liquid-NMR, solid-state NMR and Raman spectroscopies, that allowed us to confirm the presence of included water in non-emissive Cs_4PbBr_6 samples and quantify its concentration.

In summary, our work demonstrates that water can be captured within Cs_4PbBr_6 during its crystallization, justifying the difference in unit cell volumes of emissive and non-emissive crystals that was previously attributed to the presence of bromine vacancies within the emissive samples.

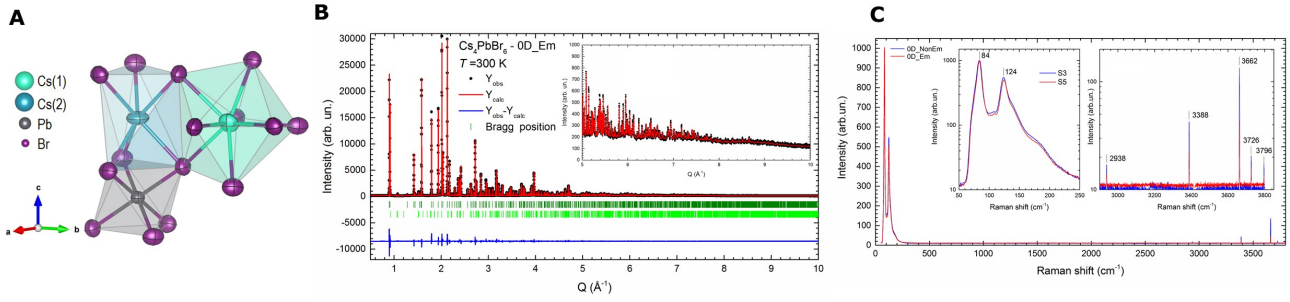

Figure 1. (a) Sketch of the coordination polyhedral in Cs_4PbBr_6 at 300 K with displacement ellipsoids drawn at the 90% probability level (as obtained by fitting the PDF data); (b) Rietveld refinement plot for Cs_4PbBr_6 (XRPD data collected at 300 K); (c) Normalized raman scattering spectra for the emissive and non – emissive Cs_4PbBr_6; the inset shows selected regions at higher magnification (logarithmic scale of intensities)

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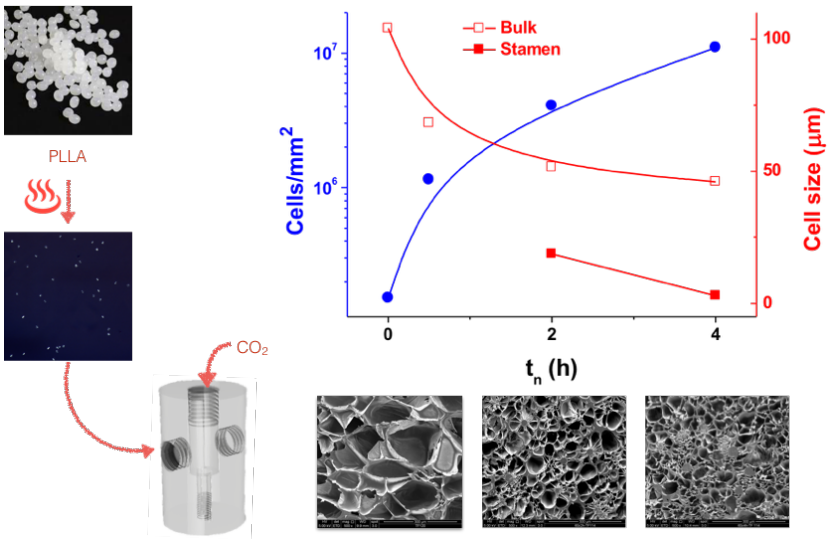
Influence of crystal nuclei in glassy Poly(L-lactic)acid on foam morphology

Alessandra Longo[a,b,c], Maria Laura Di Lorenzo [b], Ernesto Di Maio[a,c]*

[a] *University of Naples Federico II, Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Naples, 80125, Italy;* [b] *National Research Council (CNR), Institute of Polymers, Composites and Biomaterials (IPCB), c/o Comprensorio Olivetti, Via Campi Flegrei 34, 80078, Pozzuoli, Italy;* [c] *FoamLab, University of Naples Federico II, P.le Tecchio 80, 80125, Naples, Italy*



The influence of homogeneous crystal nuclei on the morphology of Poly (L-lactic) acid (PLLA) foams is detailed in this contribution.

Although PLLA has a slow crystallization kinetic, being a semi-crystalline polymer its foaming process is challenging. Growing crystals can play a dual, competitive role in physical foaming, as heterogeneous nucleation sites for bubbles but, at the same time, a high crystal fraction can hinder the expansion due to the low solubility of $scCO_2$ in the crystalline phase [2].

Annealing glassy PLLA allows the formation of a huge number of small unstable chain aggregates named homogeneous crystal nuclei which do not affect the initial crystal fraction of the polymer but can accelerate subsequent crystallization upon heating [1]. Thus, homogeneous nuclei represent the ideal way to overcome the challenge in foaming PLLA.

PLLA has been annealed at its glass transition temperature (T_g) for various nucleation times t_n = 0.5, 2 and 4 hours and then physical foamed with $scCO_2$ in a batch equipment. The effect of homogeneous nuclei has been evaluated via thermal analysis and microscopy showing an increase of the nuclei density with t_n. This reflects in the foam morphology, leading to a higher bubble density and a decrease in the cell size.

The absence of initial crystallinity of samples before foaming, together with the enhancement in the expansion ratio due to the presence of homogeneous nuclei, corroborate the advantages of exploit the homogeneous nucleation of PLLA to improve foaming of the polymer preserving its biodegradability, avoiding the addition of heterogeneous nucleating agents which could be a complicating factor for the waste disposal.

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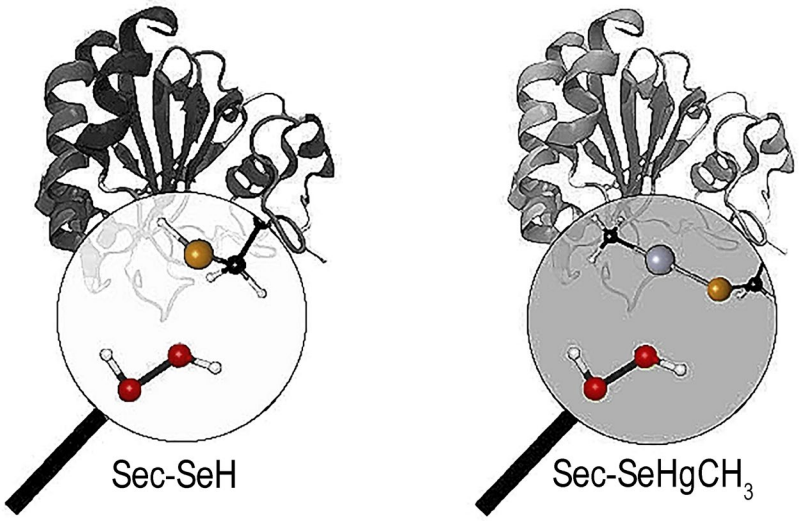
Methylmercury Binding to Selenoproteins: an Atomistic Picture From Quantum Chemistry[1]

Andrea Madabeni[a], Pablo A. Nogara[b], Marco Bortoli[a], Joao B.T. Rocha[b], Laura Orian[a]

[a] Dipartimento di Scienze Chimiche, Università degli Studi di Padova, 35131 Padova, Italy[b]Departamento de Bioquímica e Biologia Molecular, Universidade Federal de Santa Maria (UFSM), 97105-900 Santa Maria, RS, Brazil

The binding of methylmercury ($MeHg^+$) to biological thiols and selenols has long been recognized as the molecular basis of its toxicological activity. Particularly, the main targets of $MeHg^+$ have been proven to be redox active selenoproteins, deeply involved in peroxide reduction, either directly such as Glutathione Peroxidase (GPx) or indirectly such as Thioredoxin Reductase (TrxR).[2]



However, the experimental investigation of the inhibition mechanism of selenoproteins by $MeHg^+$ at the atomistic level is complicated, so far that only very recently[3] a direct evidence of the formation of a Hg-Se bond between $MeHg^+$ and the catalytically active selenocysteine (Sec) of TrxR was obtained.

The main scope of this work is to understand via Density Functional Theory (DFT) calculations how the binding of $MeHg^+$ to the chalcogen nucleus of either a cysteine (Cys) or Sec residue affects their capability to reduce peroxides, thus providing insight into the effect of $MeHg^+$ binding on peroxide reducing enzymes.

DFT mechanistic investigations for the oxidation of a free Cys and Sec, and their relative complexes with $MeHg^+$ (i.e. MeHgCys and MeHgSec) revealed how the binding of the metal to the chalcogen strongly lowers the capacity of both Cys and Sec to reduces peroxides with respect to fully deprotonated cysteinate and selenocysteinate residues. However, with respect to fully protonated residues, the metal binding promotes the peroxide reduction.

Our results indicate for the first time that $MeHg^+$ toxified enzymes might still reduce peroxides, leading to the formation of selenoxides species, thus providing physico-chemical insight into the mechanism of $MeHg^+$ toxicity and establishing as a building block in the understanding of the evolution of $MeHg^+$ toxified selenoproteins.

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Effect of non-ambient conditions on the structural and transport properties of mixed oxides for Solid Oxide Cells

Sara Massardo[a], *Davide Marchelli*[a], *Cristina Artini*[a,b], *Marcella Pani*[a,c], *Maria Maddalena Carnasciali*[a,d]

[a] *DCCI, Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso 31, 16146 Genova, Italy;* [b] *Institute of Condensed Matter Chemistry and Technologies for Energy, National Research Council, CNR-ICMATE, Via De Marini 6, 16149 Genova, Italy;* [c] *CNR-SPIN Genova, Corso Perrone 24, 16152 Genova, Italy;* [d] *INSTM, Genova Research Unit, Via Dodecaneso 31, 16146 Genova, Italy.*

Doped ceria oxides form a family of promising electrolytes that are currently investigated to be used in Solid Oxide Fuel and Electrolysis Cells (*SOFCs* and *SOECs*, respectively) working in the intermediate temperature range, due to their high ionic conductivity between 773 and 973 K. In fact, the insertion of a small amount of trivalent rare earth ions (RE^{3+}) into the fluorite-like (F) structure of pure ceria causes the occurrence of a solid solution in which Ce^{4+} ions are randomly replaced by RE^{3+} ions, and not associated oxygen vacancies are free to move through the lattice, making the $Ce_{1-x}RE_xO_{2-x/2}$ systems good oxygen ions conductors. On the other hand, when the dopant amount increases ($x > x_{max}$), different and complex scenarios may occur, mainly depending on the difference in size between the Ce^{4+} and RE^{3+} ions [1]. However, the highest values of ionic conductivity are always reached well below the x_{max} compositional limit, since C phase nanoclusters (where C is the RE_2O_3 typical structure of the smallest lanthanides) that trap oxygen vacancies grow within the F matrix with increasing x, thus affecting the ionic conductivity of the system. In the last few years, our research group undertook a comprehensive study on differently doped and co-doped ceria systems (RE≡ Gd, Sm, Lu, Nd/Tm, Nd/Dy) at non-ambient conditions [2, 3, 4], mainly focusing on the effects of high temperature on the structural and transport properties of the present oxides. In fact, investigating doped ceria systems at the typical *SOFCs* working temperatures through different techniques (x-ray diffraction by synchrotron light, impedance spectroscopy and μ-Raman spectroscopy) is fundamental to determine their effective ionic conductivity and to detect the occurrence of phase transitions that might affect the performance of the electrolytes. In particular, μ-Raman spectroscopy resulted to be a technique of choice for the study of the present systems, since it allowed to detect the presence of C-phase defect clusters growing in the F matrix even at the nanoscale [5]. To date, our research group is also performing a low temperature μ-Raman study on the present compounds, to increase the resolution of their Raman spectra. In fact, previous studies performed at room temperature on these systems, suggested the presence of hardly detectable Raman modes, partially hidden underneath the main signals, which could be revealed by lowering the temperature of the system, thus providing additional structural information on this class of compounds.
Comparative results from the analyses performed both at high and low temperature on the mentioned doped ceria systems will be given.

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Liposomes@PDA for the adsorption of methylene blue from aqueous waste

A.M. Maurelli [a], F. Lupone [a], V. De Leo [a], C. Ingrosso [b], A. Agostiano [a], L. Catucci [a]

[a] Department of Chemistry, University of Bari, Via Orabona 4, 70126 Bari, Italy; [b] CNR-IPCF, Institute for Physical and Chemical Processes, Bari unit, via Orabona 4, 70126 Bari, Italy

Polydopamine (PDA) is a mussel-inspired polymer which derives from the self-polymerization of dopamine hydrochloride (DA) in slightly alkaline conditions, and it has been demonstrated to be an excellent adsorbent material for several kinds of pollutants[1]. We prepared PDA coated liposomes and explored their adsorption capability by using methylene blue (MB) as a model compound for pollutants in aqueous waste. The considered adsorption process involves the synergistic effect of π-π stacking and electrostatic interactions[2].

Liposomes were prepared by extrusion method using membranes with a defined porosity of 200 nm. Then, they were coated with PDA by inducing the self-polymerization of DA in a buffer alkaline aqueous solution, for 24 hours and under stirring. The template-effect due to the presence of liposomes induces the polymerization at DA concentration lower than the one required for the synthesis of PDA nanoparticles[3] and allows to obtain systems about 2 μm in diameter. TEM and DLS analysis were used to monitor PDA growth over time. The polymerization yield was also evaluated exploiting the peak of absorption of the DA at 280 nm. The adsorbent capability of liposomes@PDA was investigated by evaluating the amount of MB absorbed per unit of mass of the layer of PDA (q_t). It was observed that the q_t value increases with time and with increasing MB concentrations and that the process reaches the equilibrium after 90 minutes (q_e). Moreover, it was evidenced a strong influence of the pH on the process, with the highest removal capability at pH = 8. This may be due to the change of the charge of the PDA layer at different pH. This suggestion was confirmed through ζ-potential measurements, that show a positive charge of the systems at pH = 3 and a progressively more negative charge with increasing pH values. These results agree also with the observation that the adsorbent material can be regenerated by lowering the pH from 8 to 3. Then, thermodynamic parameters have been evaluated by changing the temperature of the process.

The q_e obtained in this study are higher than several ones reported in literature for similar PDA based absorbent materials. The adsorption phenomenon, in fact, occurs mainly at the surface of the PDA layer. The structure of the liposomes@PDA allows to maximize the surface of the absorbent shell while minimizing its mass. Moreover, it was observed that these systems spontaneously precipitate after a couple of hours and they can be easily redispersed in solution with vigorous agitation. This can be useful in the optic of an easy and low-cost remotion of the adsorbent material from the treated water.

Kinetic studies were also conducted on the collected data. According to the literature, the process seems to follow a pseudo-second-order kinetic model. Finally, applying different isotherm models to the data, results show good compatibility with the Langmuir one, with the consequent suggestion that the adsorption process involves the formation of a single monolayer of MB onto the PDA surface and that the sites of adsorption can be considered homogeneous.

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Mixtures of discotic and spherical soft particles: de-mixing, liquid crystal behaviour and relative solubility

Valerio Mazzilli,[a,b*] Katsuhiko Satoh[c] and Giacomo Saielli[a,b]

[a.] *CNR Institute on Membrane Technology, Padova Section, Via Marzolo, 1 - 35131 Padova, Italy Email: valerio.mazzilli@phd.unipd.it* [b.] *Department of Chemical Sciences, University of Padova, Via Marzolo, 1 - 35131 Padova, Italy.*[c.] *Department of Chemistry, Osaka Sangyo University, Daito, Osaka, Japan.*

Liquid crystals (LCs) are materials of wide applicability in different fields.[1] Controlling the crystalline structure is a key knowledge to build reliable and competitive technologies based on such elementary units. LCs are, often, used in combination with other non-nematogenic substances to finely tune the overall properties of the material, and in this case the assessment of phases could not be easy nor straightforward. LC particles have different shapes and sizes, ranging from spheroidal to elliptic. These attributes strongly affect the phase behaviour and aggregates' properties. Therefore, it is not a simple task to determine the phase, or phases, arising from a mixture of differently shaped particles. In this work, we studied a series of mixtures, with different molar fractions, composed of discotic LC and spherical non-nematogenic particles. These mixtures were simulated with a set of coarse-grained (CG) Molecular dynamics (MD) simulations modeled using Gay-Berne (GB) and Lennard-Jones(LJ) potential for LC particles and non-LC particles, respectively. Parameters were chosen from the work of Bates and Luckhurst.[2] To evaluate the thermotropic nature of these mixtures, collections of simulations at different scaled temperatures were made in the NVT ensemble at constant packing fraction. Such mixtures were, then, probed for structural and phase information. The heterogeneity order parameter (HOP)[3], accounting for phase's separations, helped us observe the de-mixing of these two kinds of particles. The phase's assessments were studied by calculating two other parameters, well known in literature: the orientational order parameter, $\langle P_2 \rangle$, and the hexatic order parameter, $\langle \Psi_6 \rangle$. We notice that the studied systems behave differently depending on the preponderance of GB or LJ particles. The former systems undergo a nematic-to-isotropic transition, with decreasing transition temperature as the fraction of LJ solutes is increased, keeping a single phase with a relatively large amount of LJ particles dissolved. In contrast, the latter systems undergo a de-mixing of particles in concomitance with the transition to the nematic. A correlation is also observed between the orientational order parameter of the LC phase and the solubility of LJ particles within the LC phase itself. The phase-behaviour properties of such systems is summarized in the temperature-mole fraction phase diagram, depicted in the Fig. 1, where the red line represents isotropic (I) to nematic (N) transition, the blue line the N to columnar hexagonal (Col_h) and the black line the segregation of the phases inside the simulation box. The I to N transition, and its minimum will be discussed with more detail during the poster session.

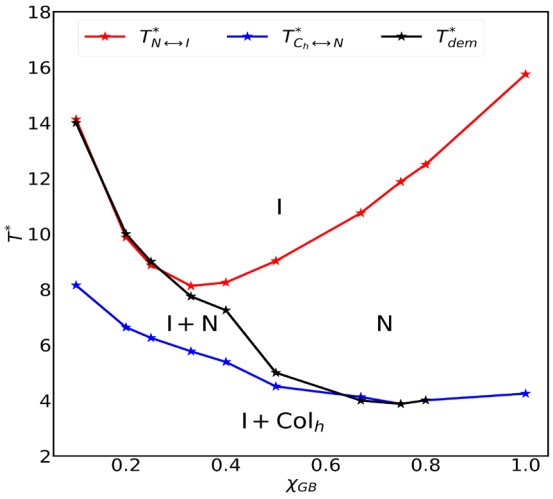

Fig 1

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Looking for Minor Phenolic Compounds in Extra Virgin Olive Oils using Neutron and Raman Spectroscopies

R. Senesi [1,2], C. Andreani [1], P. Baglioni [3], L. A. E. Batista de Carvalho [4], S. Licoccia [5], M. P. M. Marques [4,6], G. Moretti [3], A. Noce [7], R. Paolesse [5], S. F. Parker [8], E. Preziosi [1], G. Romanelli [8], A. Romani [9] and N. Di Daniele [7]

[1] NAST Centre, Physics Department, Università degli Studi di Roma "Tor Vergata", Via della Ricerca Scientifica 1, 00133 Rome, Italy.[2] CNR-IPCF Sez. Messina, Viale Ferdinando Stagno d'Alcontres 37, 98158 Messina, Italy.[3] CSGI and Chemistry Department, University of Florence, Via della Lastruccia 3, Sesto Fiorentino, 50019 Florence, Italy.[4] Molecular Physical-Chemistry R&D Unit, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal.[5] NAST Centre, Chemical Science and Technologies Department, Università degli Studi di Roma "Tor Vergata", Via della Ricerca Scientifica 1, 00133 Rome, Italy.[6] Department of Life Sciences, University of Coimbra, 3000-456 Coimbra, Portugal.[7] UOC of Internal Medicine-Center of Hypertension, Nephrology Unit, Department of Systems Medicine, Università degli Studi di Roma "Tor Vergata", Via Montpellier 1, 00133 Rome, Italy.[8] ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX110QX, UK.[9] PHYTOLAB (Pharmaceutical, Cosmetic, Food Supplement, Technology and Analysis)-DiSIA, University of Florence, Via U. Schiff, 6, 50019 Sesto Fiorentino, Italy.

Extra virgin olive oil (EVOO) is defined as a functional food with well-recognized health-beneficial properties, such as high antioxidant and anti-inflammatory capacity, due to its high content of numerous phenolic components. These characteristics depend on their structural/conformational behavior, which is largely determined by intra- and intermolecular H-bond interactions. Recent investigations [1,2] show the vibrational dynamics of isolated compounds, but in a real-life sample of EVOO their signal is overwhelmed by the major oil components, such as oleic (ca. 80%), linoleic and palmitic acids (ca. 20%) [3,4]. In this work [5], we provide a full characterization of the vibrational spectroscopic signals from commercially available EVOO samples using Inelastic Neutron Scattering (INS) and Raman spectroscopies. The spectra are dominated by CH_2 vibrations, especially at about 750 and 1300 cm^{-1} and their profiles reveal the presence of hydroxytyrosol and secoiridoids. After comparison of the spectra obtained on EVOO samples with hydroxytyrosol and other minor phenolic compounds standards, we individuated the best regions in which to look for the structure–activity information related to the minor polar compounds: at 675 and 1200 cm^{-1} for hydroxytyrosol, and around 450 cm^{-1} for all minor polar compounds used as reference, especially if a selectively deuterated sample is available. The different amounts of phenolic esters versus acids, as reflected by the relative intensities of the peaks at 1655 and 1747 cm^{-1}, show a correlation with the regional origin of the EVOO samples investigated**Nessuna voce trovata per il sommario.**.

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Theoretical Characterization of the Reduction Potentials of Nucleic Acids in Solution

Alessandro Nicola Nardi,[a] Valeria D'Annibale,[a] Andrea Amadei,[b] Marco D'Abramo[a]

[a] Department of Chemistry, Sapienza University of Rome, Rome 00185, Italy; [b] Department of Chemical Science and Technology, Tor Vergata University, Rome 00133, Italy

We present the theoretical-computational modeling of the oxidation properties of four DNA nucleosides and nucleotides and a set of dinucleotides in solutions.[1] We employed the Perturbed Matrix Method (PMM) to evaluate the vertical ionization potential and reduction potential. The method allows to describe the molecular electronic properties in complex systems through a mechanical-statistical treatment from which it is possible to extract thermodynamic properties, such as free energy. We found that the effect of the environment, in water and acetonitrile solution, is to stabilize the oxidized state of nucleobases resulting in a reduction of the energy with respect to the gas phase. Our estimates of the aqueous and gas-phase vertical ionization energies, in good agreement with photoelectron spectroscopy experiments, show that the effect of the phosphate group and of the additional nucleotide in dinucleotides is rather limited in aqueous solution. Also the reduction potentials of the nucleosides are in good agreement with respect to the available experimental data (cyclic voltammetry)[3,4] for aqueous and acetonitrile solutions.

Molecule	VIE/eV (PMM)[1]	VIE exp/eV (PES)[2]	V_{red}/V (PMM)[1]	V_{red} exp/V (CV)[3] (nucleobases)	V_{red}/V (PMM)[1]	V_{red} exp/V (CV)[4]
	Water	Water	Water	Water	Acetonitrile	Acetonitrile
Guanosine	7.98	-	1.05	1.22	1.18	1.38
Adenine	8.17	-	1.26	1.49	1.50	1.85
Thymine	8.46	8.10	1.73	1.49	1.64	2.00
Cytosine	8.49	8.10	1.87	1.62	1.79	2.03

Table 1. Calculated (PMM) and experimental (from photoelectron spectroscopy experiments, PES) vertical ionization energies (VIEs) in eV and calculated (PMM) and experimental (from cyclic voltammetry, CV) reduction potentials in V vs SHE in water and acetonitrile solutions.

Further studies are ongoing to investigate oxidation properties and charge transfer processes in more complex contests such as B-DNA and DNA quadruplex in solution.

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Superstructure effect on magnetic properties of magnesium dopped maghemite nanoparticles

Alexander Omelyanchik[a,b], Nader Yaacoub[c], Claudia Innocenti[d,f], Claudio Sangregorio[d,f], Fabio Canepa[a], Davide Peddis[a,g]

[a] Università di Genova, Dipartimento di Chimica e Chimica Industriale, nM2-Lab, Via Dodecaneso 31, I-16146, Genova, Italy[b] Immanuel Kant Baltic Federal University, Kaliningrad, Russia [c] LUNAM, Université du Maine, Institut des Molécules et Matériaux du Mans CNRS, UMR-6283, F-72085 Le Mans, France[d] Institute of Chemistry of Organometallic Compounds – C.N.R., 50019 Sesto Fiorentino, Italy[f] INSTM and Dept. of Chemistry, University of Florence, 50019 Sesto Fiorentino, Italy[g] Istituto di Struttura della Materia, CNR, 00015 Monterotondo Scalo, (RM) Italy

Magnetic iron oxides maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) in form of nanoparticles (NPs) attracted enormous attention due to their potential biomedical application. This interest is first of all caused by their tunable magnetic properties and moderate cytotoxicity. Both iron oxides have an inverted cubic spinel structure, however, the maghemite has cation vacancies in octahedral positions [1]. Missed Fe^{2+} cations make maghemite more biocompatible because the Fe^{2+} ions play a crucial in the catalytic activity of the spinel ferrite NPs. The cationic vacancies can be distributed randomly or to form a superstructure with space group $P4_132$ [2]. The effect of this superstructure on the magnetic properties of NPs still poorly documented in literature because usually the smallest particles do not reveal the superstructural features. Nevertheless, understanding this phenomenon will allow better control magnetic properties of NPs. For example, recently it was discovered that systematical doping of Mg^{2+} into vacancy sites may significantly improve magnetic properties that allowed increase magnetic heat induction during magnetic hyperthermia for cancer treatment [3].

This work sheds light on the interplay of the superstructural and magnetic properties of maghemite-based NPs. A set of maghemite and maghemite doped with small amounts of other divalent transition metals (Mg^{2+}, Zn^{2+}) was prepared with the sol-gel auto-combustion method. Manipulation of reaction kinetics through the setting of temperature regime allowed preparing NPs of the same size (~20 nm) and variating superstructural properties. Effects of doping and superstructure on magnetic properties were investigated with SQIUD magnetometry and Mössbauer spectroscopy in wide temperature and field rages.

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Supramolecular formation and deposition of chiro-optically active porphyrin-silica helices adducts.

M. Ottolini,[1] S. Bettini,[2] L. Valli[2], G. Giancane[3] M. O. Senge[4], N. Grover[4] R. Oda[5]*

[1] Department of Engineering of Innovation, Campus University Ecotekne, University of Salento, Via per Monteroni, 73100 Lecce, Italy[2] Department of Biological and Environmental Sciences and Technologies, DISTEBA, University of Salento, Via per Arnesano, 73100 Lecce, Italy [3] Department of Cultural Heritage, University of Salento, Via D. Birago, 73100, Lecce, Italy[4] School of Chemistry, Trinity College Dublin, The University of Dublin, Dublin 2, Ireland[5] CNRS Centre National de la Recherche Scientifique, Paris, France

Porphyrin derivatives exhibit excellent absorption and luminescent properties. Inorganic silica right (or left) handed nanohelices [1] can be used as chiral templates to induce optically active properties to achiral porphyrin molecules through a supramolecular approach. The possibility to build-up such 3D chiral adducts is important in the framework of chiral separation and recognition, chiral catalysis, and 3D display technology.[2]
The achiral porphyrin derivative [3] shown in Figure 1A was used as amphiphilic anchor to immobilize amine-functionalized silica nanohelices onto solid supports by exploiting weak interactions, i.e. hydrogen bonds.

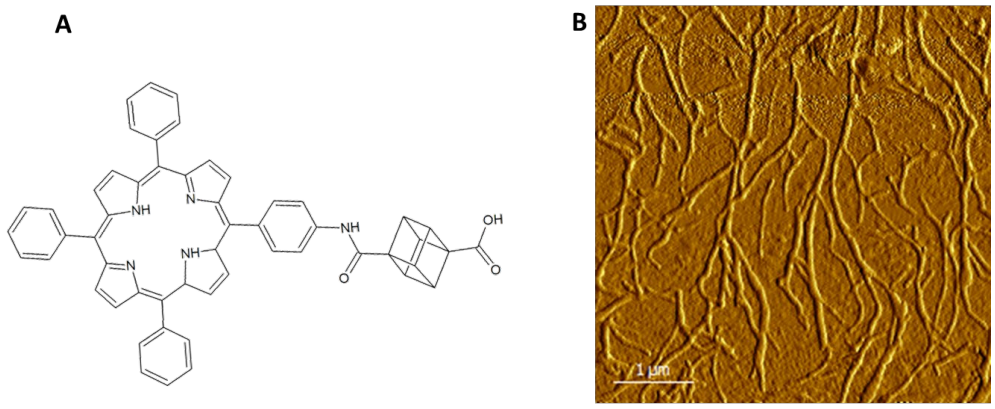

Figure 1: A) Chemical structure of achiral porphyrin derivative; B) AFM image of a LS film of nanohelices anchored by the achiral porphyrin

The obtained supramolecular adduct thin films, deposited by means of the Langmuir-Schaefer (LS) approach, resulted water-insoluble proposing such films for sensing of pollutants, toxic compounds and chiral biological molecules, such as amino acids, antibiotics, drugs, dissolved in aqueous matrices.
The LS technique induced the formation of a significant amount of organized nanohelices anchored by the achiral porphyrin in the LS films (Figure 1B) suggesting thus a chiral imprinting at the supramolecular level within the hybrid film.

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Cr(VI) Remediation Applications of Coffee derivate Carbon Nanoparticles (CNPs)

R. Pagano [a,b], M. Ottolini [c] , S. Bettini [a,b], G. Giancane [d,b] and L. Valli [a,b]*

[a] Department of Biological and Environmental Sciences and Technologies, DISTEBA, University of Salento, Via per Arnesano, I-73100 Lecce, Italy [b] Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, INSTM, Via G. Giusti, 9, I-50121 Firenze, Italy,[c] Department of Engineering for Innovation, University of Salento, Via per Monteroni, I-73100 Lecce, Italy;[d] Department of Cultural Heritage, University of Salento, Via D. Birago, 48, I-73100 Lecce, Italy.

Among contaminants, harmful heavy metals tend to accumulate and show pronounced permeation properties. They are usually derived from anthropogenic activities, mainly in industrial and agricultural areas. Among heavy metals, hexavalent chromium can be absorbed by the lung and gastrointestinal tract [1] and when internalized in the cells, it can react producing re-active intermediates capable to attack DNA, proteins and lipidic membranes, thereby affecting the cellular vitality and integrity. In this contribution, spent coffee grounds have been successfully used as a carbon source for synthetizing carbon nanoparticles (CNPs) through a simple, cheap and eco-friendly procedure according to an oxidation process (at controlled temperature) driven by hydrogen peroxide working at 200 °C and at ambient pressure for 90 min in MilliQ grade water. The CNPs were characterized by Atomic Force Microscope, fluorescence, UV-Vis absorption, FT- IR and Raman spectroscopy. The synthesized carbon materials were used for the rapid reduction of Cr(VI) to Cr(III) in aqueous media in a weak acid environment. The mechanism has been demonstrated to be ruled by the activation of CNPs surface chemical groups, which became active sites for the chemical reduction of the toxic ion [2]. Further, Mn(VI) has been reduced to Mn(II), in water, without acid activation according to data reported in the literature for other carbon based-nanosystems.

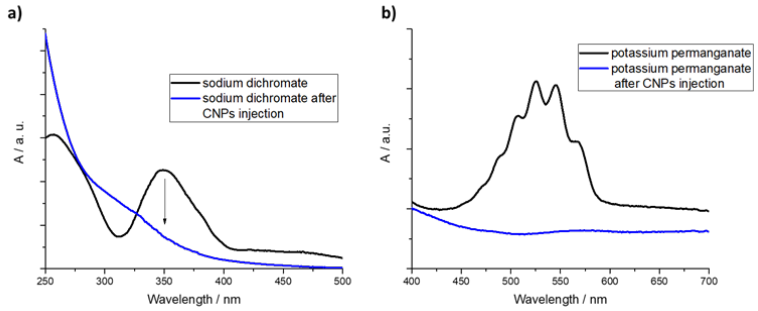

Figure 1: Spectroscopic evidence of the effect induced by CNPs on (a) dichromate and (b) permanganate solutions.

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Controlling the interphase coupling of magnetically hard-soft $SrFe_{12}O_{19}$-$CoFe_2O_4$ based nanocomposites

P. Maltoni[a], G. Barucca[b], T. Sarkar[a], G. Varvaro[c], F. Locardi[d], M. Ferretti[d], D. Peddis[c,d], R. Mathieu[a]

[a]Department of Materials Science and Engineering, Uppsala University, SE-751 03, Uppsala, Sweden; [b]Università Politecnica delle Marche SIMAU, Via Brecce Bianche 12, 60131 Ancona, Italy; [c]Institute of Structure of Matter, Italian National Research Council (CNR), 00015, Rome, Italy; [d]Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31, I-16146, Genova, Italy

Magnetic nanocomposites (NCs) have gained a lot of interest over the last years, due to the possibility to finely control and modify their features at the nanoscale, which allows to extend their applicability in a multitude of energy-related technological areas, such as permanent magnets [1]. In this regard, exchange coupled hard-soft NCs have received significant attention, as a promising strategy to achieve high magnetic performances [2]: the main challenge is to develop systems which simultaneously show a large coercivity (H_C) and high magnetization. Hereby our focus here is on the investigation of the synthesis strategy in controlling the magnetic coupling, through the optimization of the interface between two magnetic phases, $SrFe_{12}O_{19}$ (SFO) and $CoFe_2O_4$ (CFO) nanoparticles (NPs), thus achieving efficiently strongly coupled nanostructures [3,4,5]. Several samples were synthesized through a self-combustion sol-gel approach, with compositions ranging from 50/50 to 90/10 SFO/CFO w/w %, in step of 10%. In order to elucidate the synthesis method, a thermogravimetric/differential thermal analysis (TG/DTA) was performed, showing a first evidence that the reaction proceeds in a symbiotic way, where the formation of CFO after-combustion assists the evolution of SFO precursors, when CFO fraction is increased. The subsequent investigation on the inner structure of the NCs, by transmission electron microscopy (TEM), revealed that SFO NPs are in the form of platelets, with CFO nanocrystals confined between the SFO ones. The evidence of a symbiotic growth was furtherly confirmed by X-ray powder diffraction (XRPD): the crystallites´ size extracted by Rietveld refinement show an evident dependence of SFO crystallites´ size on the amount of inserted softer CFO phase. When CFO % increases, the mean size for SFO drops from 118 to 89 nm. To clarify the relationship between the morphological-structural features and magnetic coupling, the static magnetic properties of NCs were investigated at 300K using a SQUID magnetometer. The analysis of field-dependent magnetization loops shows that the two magnetic phases are homogeneously dispersed and strongly coupled. Furthermore, the switching field distributions exhibit a single reversal process of magnetization, confirming that the phases are strongly coupled. In conclusion, our study shows that the CFO grains act as nucleation sites for the SFO phase, resulting in an effect of confinement, which restricts the growth of one phase by the other. Furthermore, it is possible to control and limit the decrease of the coercivity of bi-magnetic NCs to our desire by controlling the size and distribution of the hard-soft regions, and their interface [4].
We thank the Swedish Energy Agency and Swedish Research Council (VR) for financial support.

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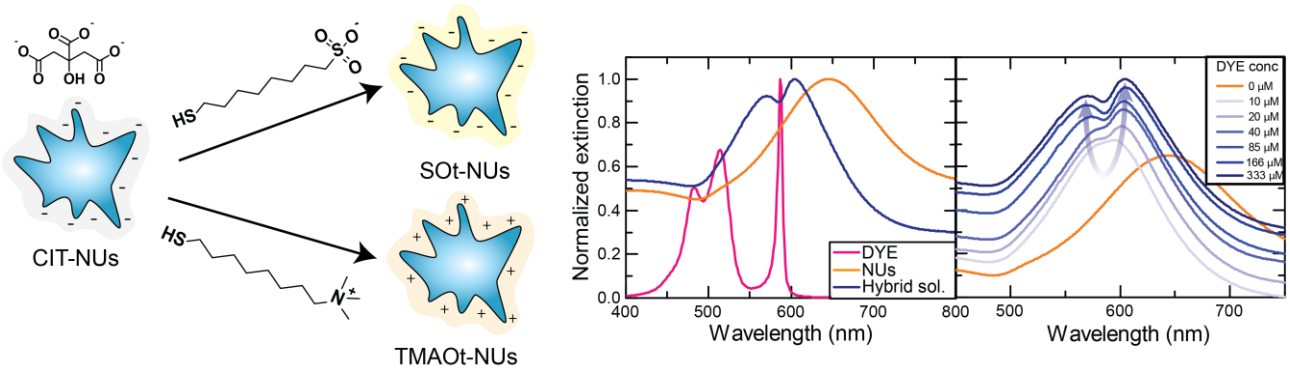
Plexcitonic engeneering: first steps to quantum technologies

A. Nicola Peruffo[a], *B. Fabrizio Mancin*[a], *C. Elisabetta Collini*[a]
Department of Chemical Sciences, University of Padova, Padova, Italy



The outcome of novel quantum technologies is one of the most challenging issue of our century. However, this burgeoning field presents some unsolved questions, like the fast damping of quantum coherences. In this framework, the coupling with the environment plays a key role and therefore it requires careful handling and precise engineering. For instance, it has been suggested that the short coherence times characterising plasmonic materials can be significantly increased through the strong coupling with an excitonic environment, giving rise to the so-called plexcitonic systems.[1,2] However, the plexcitonics field is still in its infancy and the most relevant requirements to obtain the proper coupling between plasmonic and excitonic moieties are still unclear. In this perspective, we built a large library of hybrids formed by gold nanourchins (NUs) with different capping layers (left image) and different dyes. Further morphological and spectroscopical experiments (right panel in the figure) have been performed on the samples where plexcitonic resonances were present, in order to gain a deeper knowledge about the nature of their coupling and its strength. The findings emerging from our studies have important consequences in both supramolecular plexcitonic assembling and in the understanding of their photophysical features.[3]

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Novel biocomposite for an active and biodegradable packaging material

Rebecca Pogni[a], Daniele Spinelli[b], Maria Fernandez Lobato[c], Ana Garcia Cabado[d], Vanesa Martinez Nogués[e], Raffaele Saladino[f]

[a]Department of Biotechnology, Chemistry and Pharmacy, University of Siena (Italy); [b]Next Technology Tecnotessile Prato (Italy); [c] CSIC, Madrid (Spain); [d]Anfaco-Cecopesca, Vigo (Spain); [e]Tecnopackaging, Zaragoza (Spain); [f]University of Tuscia, Viterbo (Italy)

Every year, 6-8 millions of tons of waste crab, shrimp and lobster are produced globally. In developing countries, waste shells are often dumped in landfill or the sea. In developed countries, disposal can be costly. Nonetheless shells harbor many chemicals like proteins, pigments, calcium carbonate and chitin. In this context, an innovative, active and sustainable packaging material based on chitinolytic derivatives, using marine biomass wastes have been produced. Packaging based on chitinolytic derivatives is able to tackle microbial spoilage, enhancing fish shelf life, and, in the post-consumption phase it can be used as fertilizer and microbial preservatives for plants. Furthermore lignin nanoparticles will be used as active bio filler in the preparation of the new biocomposite material. This objective is part of the FISH4FISH project* which goal is to obtain a low cost active material to be exploited for the industrial applications of fish packaging. In this way, renewable resources are exploited in a sustainable manner, promoting biobased, environmentally friendly and beneficial technologies, and creating high-performing materials for a wide range of applications.

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Optical properties of nanoparticles: finite element method simulation and experiment

Giulia Quaglia, Amalia Malina Grigoras, Loredana Latterini

Nano4Light Lab - Department of Chemistry, Biology and Biotechnology, University of Perugia, Via Elce di Sotto 8, 06123, Perugia, Italy

The growing interest in optical nanoantenna can be attributed to the ability of metal and core-shell nanoparticles to translate the concepts of radio-frequency antennas to optical frequency [1]. The strongly enhanced surface plasmon resonance of noble metal nanoparticles at optical frequencies makes them excellent absorbers as well as scatterers [2]. The plasmon resonance wavelength of metal nanoparticles is sensitive to the nanoparticle's size and shape, as confirmed by the Mie theory [3]. In particular, the possibility of tuning the localized surface plasmon resonance wavelength, in the visible to near infrared region, makes metal and core-shell nanoparticles very important and promising for the potential applications in the field of communication [4], surface-enhanced spectroscopy, harvesting solar energy [5], and in several linear and nonlinear optical processes [6-9]. In the present work, the optical properties – absorbance, scattering, dielectric function - of metal and core-shell nanoparticles have been studied through the finite-element method (FEM), that presents the advantages to give the most general solution and to be applicable to any particle shapes, groups of particles, and particles on a substrate [10]. The computational results are also supported by experimental studies.

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Development of smart polymer blends of polyethersulfone and pillararene-based PDMAEMA for selective dye removal

Anna Notti,[a] Giulia Rando,[a] Maria Rosaria Plutino.[b]

[a] Department of Chemical, Biological, Pharmaceutical and Environmental Sciences (ChiBioFarAm), University of Messina, Viale F. Stagno d'Alcontres 31, 98166, Messina, Italy; [b] Institute for the Study of Nanostructured Materials, ISMN – CNR, Palermo, c/o Dep. ChiBioFarAm, University of Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy.

Nowadays, organic dyes represent a class of emerging environmental pollutants because of their wide use in textile, leather, paper, plastic and cosmetic industries, and their chemical persistence and toxicity. As a consequence, new advanced filtration techniques have increasingly been developed for the removal of such emerging pollutants, which are difficult to remediate using conventional wastewater treatment methods [1].

In this regards, polyethersulfone (PES) is a polymer featuring excellent mechanical properties, as well as thermal and chemical stability; it has been widely used as an embedding polymer for the production of nano- and ultrafiltration membranes for water purification. New functional membranes based on PES can be easily produced by blending with other polymers, cross-linkers or nanofillers, to improve its hydrophilicity, porosity, surface properties and adsorption performances [2].

Furthermore, stimuli responsive polymers [3] represent a class of useful smart materials capable of adapting and react to the surrounding environment. In particular, PDMAEMA, poly[2-(dimethylamino)ethyl methacrylate], is a polymer sensitive to external stimuli such as temperature, pH and ionic strength, with applications ranging from therapeutic and biomedical fields to nanotechnology.

In this communication, we will report on the synthesis of innovative smart polymers, combining the responsiveness of PDMAEMA polymer and the host-guest properties of the covalently linked pillararenes [4], and the subsequent blending with PES. New blended membranes and beads, developed for the selective separation of organic dyes in wastewater treatment, were fabricated by a traditional non-solvent induced phase separation (NIPS) process. Finally, chemical-physical and morphological characterization and adsorption/release tests of organic dyes of all the synthesized precursors and polymers were determined in order to correlate polymeric structures and reactivity.

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Structure, morphology and optical properties of Eu:YPO_4 nanopowders by precipitation and hydrothermal method

Maria Luisa Saladino [a], Francesco Armetta*, Cristina Leonelli [b], Cecilia Mortalò [c]*

[a] Dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche - STEBICEF, Università di Palermo, Viale delle Scienze Ed. 17, Palermo I-90128, Italy; [b] Dipartimento di Ingegneria "Enzo Ferrari", Università di Modena and Reggio Emilia, Via P. Vivarello 10, I-41125 Modena, Italy; [c]Istituto di Chimica della Materia Condensata e di Tecnologie per l'Energia-ICMATE, CNR, Corso Stati Uniti 4, I-35127 Padova, Italy.

In recent decades, rare earth (RE) doped orthophosphates have been extensively studied because they are promising hosts for the emission produced by RE^{3+} ions. Their very low water solubility, high thermal stability and high quantum efficiencies are advantageous for many applications such as lasers, LEDs, luminescent screens, scintillators, solar cells, optical fibers and bio-imaging.
Among the rare earth orthophosphates, the yttrium orthophosphate doped with europium (Eu:YPO_4) is one of the most studied because it is an important commercial red phosphorus, used in color television sets, in cathode ray tubes and in high-pressure mercury lamps [1-2]. The Eu:YPO_4 nanopowders are much more versatile and easier to obtain than single crystals as well as can be used as they are, deposited on surfaces, sintered to obtain polycrystalline ceramics of various shapes and sizes, or dispersed in polymeric materials to obtain nanocomposite materials.
In this work the synthesis of Eu:YPO_4 nanopowders by precipitation followed by an hydrothermal treatment is reported.
Thermogravimetry, X-ray Diffractometry, Infrared Spectroscopy and Scanning Electron Microscopy (SEM) and Transmission (TEM) were used to study the formation of nanopowders and to evaluate structural and morphological properties. This information was used to optimize and modify the synthesis strategy. The optical properties were studied by luminescence spectroscopy and were related to the structural properties, shape and size of the particles.
Results showed that at least 12 hours of hydrothermal treatment are required to obtain crystalline particles, since a mixture of amorphous and crystalline phases is obtained for shorter times of treatment.
The morphology of the particles changes according to the treatment time, in fact the nanopowders obtained at 8h and 18h are constituted by rod-shaped particles with a length of about 40nm and a thickness of 11nm, while those obtained at 48h from shaped particles to rice grains with a length of 24nm and a thickness of 14nm.
In all the samples, europium is well distributed in the crystalline structure of the particles. The nanopowders showed an intense orange emission and the emission bands typical of Eu^{3+}. The intensity of the emission increases with the treatment time increase and the splitting of the transitions changes both as a function of the treatment time and the water content, certainly also influenced by the different morphology.

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Structure and Dynamics of Crystalline Carbimazole by NMR Crystallography and Relaxometry

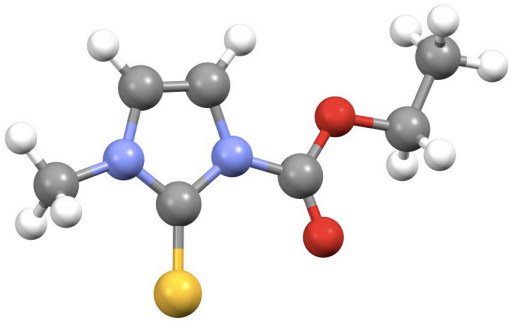
Andrea Scarperi[a], *Giovanni Barcaro*[b], *Aleksandra Pajzderska*[c], *Francesca Martini*[a,d], *Elisa Carignani*[a,e], *Marco Geppi*[a,d]

[a] *Department of Chemistry and Industrial Chemistry, University of Pisa, via G. Moruzzi 13, 56124 Pisa, Italy;* [b] *Institute For Chemical And Physical Processes, Italian National Council for Research, CNR/IPCF, via G. Moruzzi 1, 56124 Pisa, Italy;*[c] *Department of Radiospectroscopy, Faculty of Physics, Adam Mickiewicz University, Uniwersytetu Poznanskiego 2, 61-614 Poznan, Poland* [d] *Center for Instrument Sharing, University of Pisa (CISUP), 56126 Pisa, Italy* [e]*Institute for the Chemistry of OrganoMetallic Compounds, Italian National Council for Research, CNR/ICCOM, via G. Moruzzi 1, 56124 Pisa, Italy;*

Molecular dynamics and structural characteristics of a solid drug strongly affect its pharmaceutical properties and release profiles. Solid State NMR (SSNMR) has been proved to be a very important technique in the study of pharmaceuticals, allowing many different experiments to be performed in order to obtain important information on dynamic and structural properties on a broad space and time range [1, 2].

In the last two decades, the combination of solid state NMR, diffractometric techniques and computational methods has been recognized as a powerful tool in the investigation of the structure of crystalline solids, and "NMR Crystallography" is seen as a rapidly maturing subject area in the crystallographic community [3,4].

In this work, the dynamic and structural properties of the crystalline form of carbimazole, a prodrug used in the treatment of hyperthyroidism, have been investigated in detail. The combination of DFT calculation with ^{13}C MAS, ^{1}H CRAMPS, ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H DQSQ experiments has allowed the elucidation of the drug crystal structure, resolving ambiguities in diffraction-derived structures present in literature. The measurement of spin-lattice relaxation times of ^{1}H and ^{13}C nuclei at variable temperatures enabled the detailed characterization of the dynamic processes that the carbimazole molecule undergoes in the crystal lattice.



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Design of mesostructured bifunctional catalysts for CO_2 conversion to dimethyl ether

F. Secci[a], C. Cara[a], E. Rombi[a], M. Sanna Angotzi[a], S. Lai[b], K. Skrodczky[c], N. Pinna[c], M. Mureddu[b], C. Cannas[a]

[a]Department of Chemical and Geological Sciences, University of Cagliari, Monserrato (CA), Italy. [b]Sotacarbo SpA, Carbonia (SU), Italy. [c]Department of Chemistry, Humboldt University, Berlin, Germany.

CO_2 is widely recognised as the main cause of greenhouse effect, causing global warming and climate change. With the aim to reduce CO_2 emissions, during the last decades, several strategies have been developed for the capture, utilization and storage of carbon dioxide (CCUS). This work focuses on the development of bifunctional catalysts for the conversion of CO_2 into dimethyl ether (DME), a fuel with no collateral emissions other than CO_2 and H_2O, a high cetane number and chemical-physical properties similar to LPG. DME is obtained from the reaction of CO_2 with H_2 through two subsequent reactions. The first one is the CO_2 reduction with H_2 to obtain methanol; this reaction is promoted by Cu-based catalysts like $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/ZrO_2$. The second one is the dehydration of methanol to DME, catalysed by solid acidic catalysts, such as zeolites and γ-Al_2O_3 [1].

In this work three different types of mesostructured acidic catalysts were synthesized: Al-SiO_2 (Al-SBA-15, Al-MCM-41), Zr-TiO_2 and γ-Al_2O_3. These materials were tested for methanol dehydration and used as supports for the Cu-based redox phase, to obtain composite materials to be used as bifunctional catalysts. Mesostructured matrix should limit the growth of redox phase nanoparticles inside the mesopores, assure a high dispersion due to the high surface area, leading to a high contact area between the two phases and, thus, granting in principle superior catalytic performances.

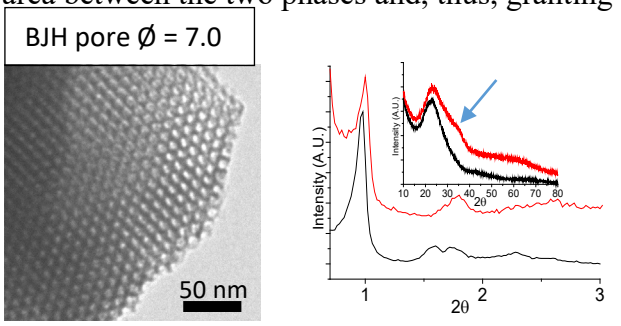

Figure 1. TEM and XRD of Al-SBA-15 (black) and composite (red)

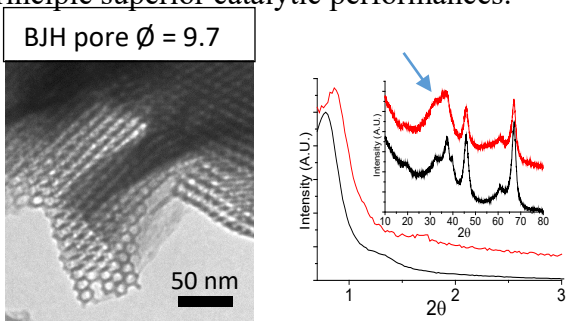

Figure 2. TEM and XRD of γ-Al_2O_3 (black) and composite (red)

All mesostructured systems were synthesized via the Sol-Gel method, either through an Evaporation-Induced Self-Assembly (EISA) or a solvothermal approach, and characterized by XRD, TEM and N_2 physisorption. Acidic sites characterization was performed by calorimetry and FTIR spectroscopy using pyridine as a probe molecule. The catalysts were eventually physically mixed with a $Cu/ZnO/Al_2O_3$-based commercial redox catalyst and tested in a bench-scale plant with a fixed bed reactor for CO_2 conversion to DME. Mesostructured supports were used to disperse the $CuO/ZnO/ZrO_2$-based redox phase by a wet impregnation method combined with a self-combustion process or by a two-solvents impregnation strategy. The obtained bifunctional catalysts were characterized by PXRD, N_2 physisorption, TEM and HRTEM in order to determine the most promising synthetic conditions in terms of dispersion and nanosize of the active phase and textural properties of the corresponding composites.

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ATR-FTIR difference spectroscopy: a powerful and rapid approach for monitoring substrate consumption and catabolite release during dark fermentation of hydrogen-producing bacteria

Paola Semeraro[a,b], Adelfia Talà[a], Maria Tufariello[c], Pietro Alifano[a], Ludovico Valli[a,b], Livia Giotta[a,b]

[a]Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, S.P. Lecce-Monteroni, I-73100, Lecce, Italy; [b]Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Unità di Lecce, S.P. Lecce-Monteroni, I-73100, Lecce, Italy; [c]National Research Council-Institute of Sciences of Food Production (ISPA), S.P. Lecce-Monteroni, I-73100 Lecce, Italy

Different facultative and obligate anaerobic bacteria can induce a microbial conversion of waste biomass through dark fermentation, leading to the generation of different catabolites, including biological hydrogen [1]. Since several complex biochemical pathways, influenced by various factors, are involved [2], a fast tracing of substrate consumption and relative products is a critical issue to assess the efficiency of fermentative processes and to optimize the operating conditions.
Fourier Transform Infrared (FTIR) spectrometry is a versatile and non-destructive technique which is in line with the principles of Green Chemistry [3] since allows to save reagents and materials for sample treatment steps, usually not needed. Furthermore, the attenuated total reflection (ATR) sampling mode and the difference approach allow to identify and even quantify individual component contribution in complex mixtures. This approach has been recently applied to study thin films of organic molecules [4], membrane proteins and even bacterial cells [5].
In this study, we report on the application of the ATR-FTIR difference technique to the characterization of culture media to study simultaneously the consumption of substrates by bacteria and the release of major catabolites during microbial growth. Specifically, the growth media after 24 hours fermentation of Enterobacter cloacae and Klebsiella aerogenes were analyzed and compared. The frequency and intensity of negative bands in difference spectra enabled to assess the complete glucose consumption in anaerobic fermentative processes by both bacterial populations, with no indication of a significant maltose uptake, demonstrating that malt extract is not efficiently metabolized by bacteria in the anaerobic growth conditions adopted.
On the other hand, the appearance of positive signals in the difference spectra pointed out the predominant formation of alcohols and the scarce production of short chain fatty acids during the fermentative process.

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Gellan gum-based microgels as a promising tool for paper preservation

Leonardo Severini [a], *Benedetta Di Napoli* [a, b], *Silvia Franco* [b], *Manuel Tumiati* [a], *Elena Buratti* [b], *Mattia Titubante* [a], *Valentina Nigro* [b], *Nicoletta Gnan* [b], *Laura Micheli* [a], *Barbara Ruzicka* [b], *Claudia Mazzuca* [a], *Roberta Angelini* [b], *Mauro Missori* [b], *Emanuela Zaccarelli* [b]

[a] *Department of Chemical Science and Technologies, University of Rome "Tor Vergata", Via Della Ricerca Scientifica 1, 00133 Rome, Italy;* [b] *Institute for Complex Systems, National Research Council (CNR-ISC) and Department of Physics, Sapienza University of Rome, Piazzale A. Moro 2, 00185 Rome, Italy*

Since most of the cultural heritage is preserved on paper material, it is essential to develop appropriate conservation strategies. Indeed, the main component of these artifacts is cellulose, that during aging undergoes irreversible degradation processes [1]. Moreover, pollution and water-soluble substances arising from cellulose degradation accelerate the aging processes, thus contributing to reduce the paper sample lifetime, leading to a decrease in paper stability and color changes. Wet cleaning that is a common restoration procedure can be efficiently ensured by opportune hydrogels [2-4]. Among those reported in literature, rigid hydrogels (macrogel) based on the deacylated polysaccharide Gellan gum and calcium acetate (Gg), as effective paper cleaning agent, has been widely characterized. Knowing in depth its behavior, characteristics and its effects on paper material, the use of Gellan gum based microgel particles, as innovative paper cleaning agent to improve the efficiency of current cleaning procedures, was proposed for the first time. Compared to established protocols (hydrogels), these colloidal particles, having reduced size can penetrate inside paper's pores and carry out their cleaning action in a shorter amount of time (few minutes). Moreover, experimental results obtained show a higher cleaning efficiency of proposed Gellan microgels (respect to Gellan gum hydrogel and water bath), on two different kind of paper materials, that differ in period of manufacture and constituent raw materials. In detail, non invasive and micro-invasive techniques like SEM, FTIR-ATR and UV-Vis reflectance spectroscopy and HPLC demonstrate that they are able to remove degradation products of cellulose performing an overall whitening action on the paper material, without altering the mechanical properties of samples. It is important to point out that this is the first application of microgels particles in cultural heritage field.

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Biocide-free sol-gel based hydrophobic coatings for marine fouling release applications: from chemical synthesis to biological function.

Annamaria Visco[a,b], Silvia Sfameni[a,c], Cristina Scolaro[a], Simone Cappello[d], Maria Rosaria Plutino[c]

[a] Dept. of Engineering, University of Messina, C.da Di Dio, 98166 Messina, Italy[b] Institute for Polymers, Composites and Biomaterials CNR IPCB, Via Paolo Gaifami 18, 9-95126 Catania, Italy[c] Institute for the Study of Nanostructured Materials, ISMN – CNR, O.U. Palermo, c/o Department of ChiBioFarAm, University of Messina, Viale F. Stagno d'Alcontres 31, Vill.S.Agata, 98166 Messina, Italy[d] National Research Council (CNR) – Institute for Biological Resources and Marine Biotechnology (IRBIM), Via S. Raineri 86, 98122 Messina, Italy

Due to the limitations involved in the use of biocides in antifouling marine systems, several technologies have been developed to produce new coatings aimed to interfere directly with the adhesion of microorganism as a result of topography or surface chemistry. It is well known that coatings based on suitable silanes provide an efficient approach for the hydrophobic and antifouling treatment of surfaces. In the present work, functional hydrophobic hybrid coatings (topcoats) were deposited on surfaces using sol-gel technology. In particular, it has been seen that functional groups in organic silanes such as long-chain alkyl or fluorinated alkyl have a significant influence on surface wettability. Furthermore, the hydrophobic behavior of functionalized coatings has been improved by introducing an intermediate layer of tiecoat between the primer and the topcoat, further decreasing its wettability with water, and making therefore such coatings ideal for the development of antifouling paints. The sol-gel mixtures were characterized by NMR spectroscopy, FT-IR spectroscopy, Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA), while the 3D surface morphology of the coated glass slides was studied by optical microscopy. Contact angle analysis and mechanical pull-off test were carried out to measure the adhesive power of the coating against a metal substrate, typically used in the nautical sector. Finally, bacterial adhesion tests and microbiological experiments, carried out in different conditions, were useful to demonstrate that the newly prepared coatings reduce the rate of bacterial adhesion through fouling release mechanism.

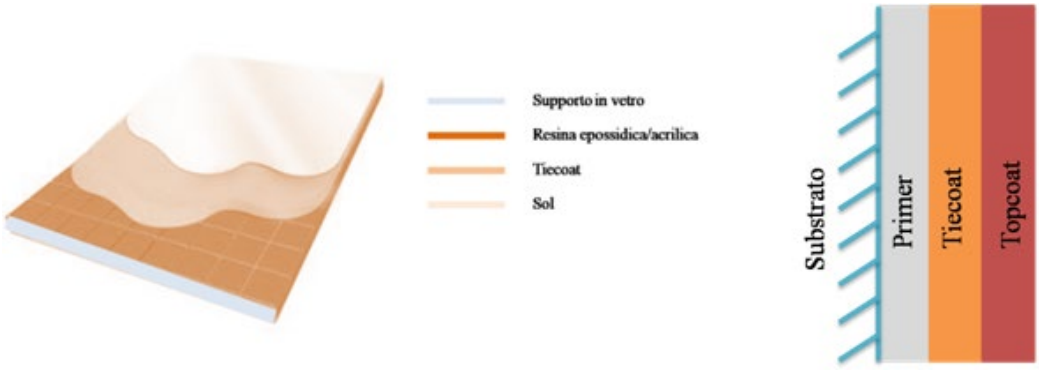

Figure- Multi-layer deposition of functional coatings on the surface

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The simultaneous binding of two duplex/quadruplex aptamers to human α-thrombin: structure and dynamics

Romualdo Troisi[a], Nicole Balasco[b], Andreas Santamaria[a], Luigi Vitagliano[b] and Filomena Sica[a]

[a] Department of Chemical Sciences, University of Naples Federico II, Naples, Italy; [b] Institute of Biostructures and Bioimaging, CNR, Naples I-80134, Italy.

Oligonucleotide aptamers, short DNA or RNA sequences that bind to their target with high affinity and specificity, are extensively used to modulate the function of most of the factors involved in the coagulation pathway. A particular case is that of the anticoagulant aptamers able to recognize the human α-thrombin (thrombin) by binding the two electropositive regions, known as exosites I and II, lying on the opposite poles of its surface [1]. One of the most extensively studied anticoagulant aptamer is TBA, a 15mer oligonucleotide recognizing the exosite I by adopting an antiparallel G-quadruplex structure [2]. Recently, the interest of researchers moved on a new class of oligonucleotides in which the addition of a duplex-forming sequences to a G-quadruplex module results in an improvement of the binding properties [3,4]. Among them, NU172 possesses a high anticoagulant activity and is the only anti-thrombin aptamer currently evaluated in Phase II of clinical trials [5]. Another interesting duplex/quadruplex aptamer is HD22_27mer that recognizes thrombin exosite II with very high affinity but without exerting a potent antithrombotic activity [6].
Great attention has been paid to the study of the effects of the simultaneous binding of two aptamers on the two exosites of thrombin. In particular, it was found that the aptamer binding to exosite II increases the binding affinity of another aptamer to the exosite I, and vice versa [7].
We investigated the simultaneous binding of NU172 and HD22_27mer aptamers by combining a structural and dynamics approach [8]. The crystal structure of the ternary complex provides a detailed view of the simultaneous binding of these aptamers to the protein, inspiring the design of novel bivalent thrombin inhibitors. Molecular dynamics studies point out the cooperation between the binding at the two exosites. In particular, the binding of an aptamer to one of the exosites reduces the intrinsic flexibility of the other exosite that preferentially assumes conformations similar to those observed in the bound state. This behavior is reflected in a significant increase of the anticoagulant activity of NU172 when the inactive HD22_27mer is bound to exosite II, providing a clear evidence of the synergic action of the two aptamers.

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Zn-based catalysts for CH_3OH synthesis from CO_2

Ticali P.[a], Morandi S.[a], Borfecchia E.[a], Salusso D.[a], Bordiga S.[a], Ahoba-Sam C.[b], Olsbye U.[b], Ramirez A.[c]*

a Department of Chemistry, NIS and INSTM Centres, University of Turin, Via P. Giuria 7, Turin, 10125, Italy b SMN Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, N-0315 Oslo, Norwayc KAUST Catalysis Center (KCC), Advanced Catalytic Materials, King Abdullah University of Science and Technology, Thuwal 23955, Saudi Arabia

** Presenting author.*

Nowadays, the usage of fossil fuels represents the main source of CO_2, a greenhouse gas responsible for the increment of global warming. The single C atom in CO_2 can be reused via catalytic processes exploiting the capability of certain materials of reducing carbon dioxide to hydrocarbons and/or olefins, by means of high temperature and pressure. This goal can be achieved using a bifunctional catalyst to convert CO_2 in organic molecules. The final goal is the development, optimisation and upscaling of bifunctional catalysts to convert CO_2 into methanol and then into hydrocarbons. This type of catalyst is made up of a metal oxide phase, employed in CO_2 conversion to methanol, and a selective zeolite, for methanol-to-hydrocarbons process. Several metals/oxides have been reported to be active for CO_2 hydrogenation including Pd-based and Zn/ZrO_2-based catalysts[1,2]. This work is focused on the characterisation and testing of bifunctional catalysts involved in methanol synthesis, based two different catalysts: $ZrZnO_X$ and $PdZn/ZrO_2$.

We analysed three $ZrZnO_X$ samples with different Zn loading prepared by co-precipitation of ZrN_2O_7 and $Zn(NO_3)_2$ with $(NH_4)_2CO_3$ and then calcined at 500 °C. $PdZn/ZrO_2$ was prepared using a solution of palladium acetate and zinc acetate as precursors and then they were used to impregnate ZrO_2 obtained from $Zr(OH)_4$. Textural, structural and morphological characterisation of the catalysts were achieved by means of BET analysis, powder X-ray diffraction (PXRD), X-ray absorption spectroscopy (XAS) and electron microscopy. While the study of surface was performed by probe molecules adsorption followed by FT-IR spectroscopy (i.e. CO, CO_2 and H_2).

According to structural characterisation of $ZrZnO_X$ samples, Zn is partially included in ZrO_2 structure. XAS results reveal a tetragonal-like ZrO_2 structure and this is only partially confirmed by a PXRD refinement. Indeed, increasing Zn loading, Zn could be stacked inside zirconia stabilising ZrO_2 in a tetragonal structure and, at higher concentration, it segregates generating a ZnO phase. The FT-IR spectra acquired during H_2 adsorption from room temperature up to 400 °C show the presence of oxygen vacancies. The presence of oxygen vacancies generated by the ZnO phase might be the key step for CO_2 adsorption and activation on the metal oxide phases, the first step for its hydrogenation to CH_3OH[3].

As for $PdZn/ZrO_2$, FT-IR and XAS show the presence of Pd-Zn alloy on ZrO_2 support. To study surface species in $PdZn/ZrO_2$, CO can be used because of its high sensitivity. After reduction at 400 °C in H_2, CO adsorbs only on Pd^0 at room temperature (RT). The absence of peaks below 2000 cm^{-1} (Fig.1), characteristic of $Pd(CO)_X$ species, proves the presence of a Pd-Zn alloy, which has been demonstrated to be directly responsible of the initial high CO_2 conversion.

This project, named COZMOS[4], has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 837733.

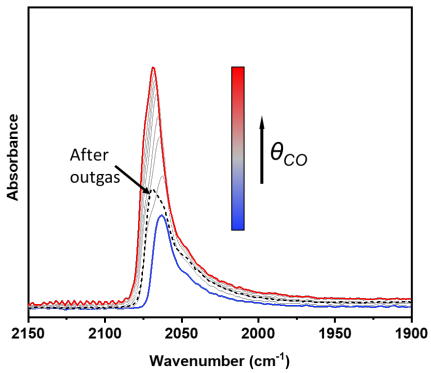

Fig. 1 - CO adsorption at RT on reduced $PdZn/ZrO_2$ at increasing CO coverage (θ_{CO})

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Testing the "sand in the gearbox" model: effects of antimicrobial peptides on the fluidity of the membranes of live *E. coli* cells

C. Troiano[1], F. Riccitelli[1], M.R. Loffredo[2], M. L. Mangoni[2], Y. Park[3], S. Bobone[1], L. Stella[1]

[1] Department of Chemical Science and Technologies, University of Rome Tor Vergata, 00133, Rome, Italy;[2] Laboratory affiliated to Pasteur Italia-Fondazione Cenci Bolognetti, Department of Biochemical Sciences, Sapienza University of Rome, Rome, Italy; [3] Department of Biotechnology, Chosun University, 501-759 Gwangju, Korea.

Antimicrobial peptides (AMPs) represent a promising class of compounds to fight resistant infections. In most cases, they kill bacteria by making their membrane permeable. We have shown that bacterial killing requires complete coverage of the membrane surface by bound peptides (10^7 bound molecules per cell) [1, 2]. Therefore, it is possible that accumulation of the peptides on the cell surfaces causes other phenomena such as perturbation of the fluidity of the cell membranes, a mechanism that has been termed "sand in the gearbox". We have studied such effects by labeling the membranes of live *E. coli* cells with three fluorescent probes, DPH, Laurdan and Pyrene. These probes position at different depths in the bilayer and allow monitoring bilayer viscosity (by fluorescence anisotropy), water penetration (by spectral shifts) and lateral lipid mobility (by excimer formation), respectively. These studies indicated that the cathelicidin AMP PMAP-23 causes a significant increase in membrane rigidity. This effect could contribute to the antimicrobial activity of AMPs, by affecting the function of membrane proteins, which is strongly dependent on the physico-chemical properties of the bilayer.

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Dopamine-based polymers: chemical and physical characterization of a biological approach to polymerization

Maria Varsalona [a,b], Rossella Labarile [a,b], Danilo Vona [a], Gabriella Buscemi [a,b], Matteo Grattieri[a,b], Angela Agostiano [a,b], Gianluca Maria Farinola [a], Massimo Trotta [b]

[a]Dipartimento di Chimica, Università degli Studi di Bari, via Orabona 4, 70125, Bari, Italy; [b]*CNR-IPCF Institute for Physical-Chemical Processes, via Orabona 4, 70125, Bari, Italy*

The purple non sulfur photosynthetic bacterial strain *Rhodobacter sphaeroides* (*R. sphaeroides*) R-26 is able to growth in a medium both aerobic and photoeterotropically.
Dopamine (DA) is a neurotransmitter that self-polymerizes into polydopamine (PDA), a synthetic analogue of melanin [1] of great interest in organic and bioinorganic electronics.
The self-polymerization of dopamine in aerobic and anaerobic environment is investigated in presence and absence of the photosynthetic bacterium.
The role of the bacterium [2, 3] on the PDA formation [4, 5] and the structure of the obtained polymer were investigated by several spectroscopic and imaging techniques.

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Therapeutic peptide nanostructures

Gianfranco Bocchinfuso,[a] Francesca Cavalieri,[a,b] Rita Cimino,[a] Marco Savioli,[a] Elisabetta Bianchi,[c] Hilda Garay Peres,[d] Mariano Venanzi[a]

[a]PEPSA-LAB, Dip. Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", Roma, Italia[b]School of Science, RMIT University, Melbourne, Australia. [c]Peptide and Small Molecule R&D Department, IRBM SpA, Pomezia, Italy.[d]Center for Genetic Engineering and Biotechnology, Havana, Cuba.

Peptides have unique advantages with respect to other polymeric materials: i) they are biocompatible; ii) their structural and dynamical properties can be finely tuned by proper selection of amino acid composition and sequence; iii) they are chiral compounds, so that chiral selectivity is intrinsically endowed; iv) their amino acid constituents can be easily engineered to extend the chemical toolbox beyond the twenty metabolic residues. It should be emphasized that the progresses of synthetic peptide chemistry made large scale production and high-standard purification of peptide-based compounds cost-effective.

Most importantly, peptides are naturally programmed to give rise to hierarchical self-assembly (HSA), so that the 3D arrangement of peptide-based architectures is determined level-by-level from the specification of the peptide sequence (primary structure), to the achievement of secondary ordering (helices, turns, sheets) and tertiary arrangements (coiled-coils, fibrils, tapes, rods, nanotubes). Non covalent assembly of tertiary structures (quaternary level of structure) paves the way for the construction of complex architectures endowed with specific functionalities.

Among the nanostructures formed by therapeutic peptides, there are nanofibrils (interactions with cells, scaffolds for tissue engineering), gels (tissue reconstruction, scaffolds), nanoparticles (drug delivery, bioimaging, biosensing), nanotubes (cross-membrane conduits, scaffolds).

The tunability of peptide nanostructures is, in its essence, due to the unique structural properties of the amino acid building blocks. They have the same basic skeletal constrain, i. e. the peptide bond forcing the 'core' of the residue to attain a rigid planar configuration, and the same topological motif, i.e. the 3D arrangement of the knots linking the amide planes determined by the Cα side-chain groups. The latter is determined by the interplay and delicate balance of the interactions stabilizing the peptide structure, i.e. electrostatics for polar or charged residues (Lys, Glu, Asn, Ser), dispersion forces for nonpolar groups (Gly, Ala, Leu), π-π stacking interactions for aromatic residues (Phe, Tyr, Trp).

There are however some harsh limitations to the development of peptide drugs. Peptides suffer from instability and after administration are usually rapidly degraded by enzymes under physiological conditions. Additionally, bioavailability and unfavourable immune response limit their use in vivo.

Self-assembly is regarded as one of the most promising approach to obtain highly stable peptide-based materials for therapeutic applications. Indeed, nanostructured therapeutic peptides have shown higher stability, improved blood circulation time, better targetability and bioavailability, resulting in therapeutic performance superior to single peptide molecules. Besides that, the dynamic nature of self-assembled nanomaterials makes easier the reversible disassembling of nanostructures under physiologically sustainable conditions.

In this contribution, we highlight some fundamental issues of therapeutic peptide self-assembly, discussing the aggregation properties of a lipopeptide used in the therapy of diabetes type I (Semaglutide) and an anticancer peptide compound presently under phase 2 clinical trial (CIGB552).

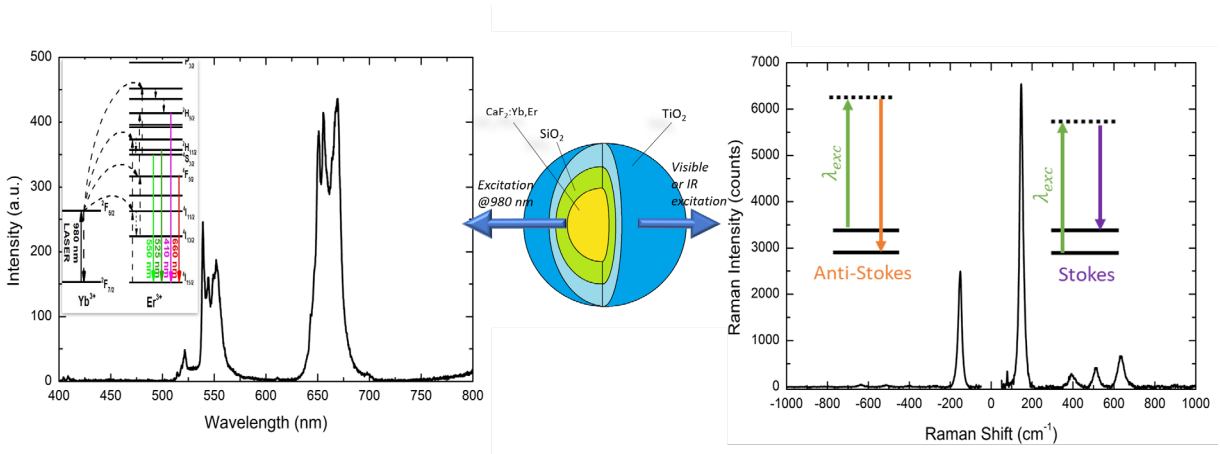
From a fundamental point of view, this contribution aims to face two very basic questions: i) how HSA is affected by secondary structure modifications, and ii) how the morphology of peptide nanostructures is determined by the self-assembly properties of peptide building blocks in a given environment.

Optical thermometry at the nanoscale using $CaF_2:Yb^{3+}$, $Er^{3+}@TiO_2$ nanoparticles

Veronica Zani [a], Chiara Cressoni [b], Giacomo Lucchini [b], Danilo Pedron [a], Roberto Pilot [a], Adolfo Speghini [b], Raffaella Signorini [a]

[a] LASPEN Research Group, Department of Chemical Science and INSTM RU Padova, University of Padova, Via Marzolo 1, Padova, Italy; [b] Nanomaterials Research Group, Department of Biotechnology and INSTM, RU of Verona, University of Verona, Strada le Grazie 15, Verona, Italy

Temperature is a very important parameter to consider in real systems, in technological devices and in biomedical applications [1]. The evaluation of temperature at the nanoscale requires both high spatial resolution and high precision, demanding for new materials and measurements techniques. In this context, the measurement of temperature not requiring a direct contact between the probe and the system is very advantageous. Optical techniques exploiting luminescence and Raman scattering are very promising as non-contact techniques, despite the spatial resolution being diffraction-limited.
Alkaline-earth fluorides activated with lanthanide ions are strongly luminescent in the optical region (UV, visible and near infrared, NIR) and some lanthanide emissions are sensitive to variation of the temperature [2]. For instance, the relative intensities of some Er^{3+} ions emission bands in the green region are strongly dependent on the temperature, directly connected to the change in population of the excited states, that are thermally populated according to the Boltzmann law.
An important feature of a Raman thermometer is the occurrence of intense Raman bands close to the Rayleigh line. Using the ratio of Stokes and anti-Stokes Raman bands, excited in the visible or in the NIR regions, the local temperature can be measured. TiO_2, in anatase form, is a promising material characterized by an intense and well defined Raman band around 140 cm^{-1}, showing high temperature sensitivity [3].
This communication presents a new nanostructured optical thermometer with double thermometric functionality, based on both luminescence and Raman scattering, involving nanoparticles (NPs) with a core-shell architecture. The NPs consist of a Yb^{3+}, Er^{3+} codoped CaF_2 core, covered with a first shell of amorphous SiO_2 and a second shell of TiO_2 anatase. The NPs show a strong upconversion emission in the visible upon NIR excitation. Stokes and anti-Stokes Raman bands, excited in the visible or in the NIR regions, allow evaluating the temperature, with a high thermal sensitivity and low temperature uncertainties, estimated in few degrees.



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Active and monitoring materials for the environmentally safe storage and exhibition of works of art

Maria Paola Staccioli [a,b], Valerio Serpente [c], Daniele M. Trucchi [c], Marco Girolami [c], Cristina Riccucci[a], Gabriella Di Carlo [a]

[a] Consiglio Nazionale delle Ricerche - Istituto per lo Studio dei Materiali Nanostrutturati – Area della Ricerca Roma1, [b]Sapienza Università di Roma, Dipartimento di Scienze della Terra- Piazzale Aldo Moro 5, 00185 Roma, [c]Consiglio Nazionale delle Ricerche - Istituto di Struttura della Materia– Area della Ricerca Roma1

The internal environment in museum buildings is critical for the conservation of collections. Granting the optimal environmental conditions around the art objects help to minimize the pollutants amount in the microclimate within the storage items and the emissions of the packaging materials (wood, paperboard, glue, etc.) thus eliminating the need for periodical interventions. The conservation approach comprising the policies and practices taken to assure the protection of cultural heritage from environmentally induced damage in known as Preventive Conservation.
It is therefore important, as part of the Preventive Conservation, both to monitor the environment and, where necessary, to mitigate the most dangerous pollutants' concentration. Several Passive Sampling Devices (PSDs) and monitoring systems are available for monitoring gaseous pollutants, especially those dangerous for human health. Nevertheless, the risk connected with these pollutants varies depending on whether they are in contact with work of arts or with human beings. Easy to use sensors for monitoring those pollutants that are more dangerous for the works of art are still not available, since the market is focused on the purification of the indoor air from the pollutants affecting human health.
Within the H2020 Project APACHE (Active & intelligent PAckaging materials and display cases as a tool for preventive conservation of Cultural Heritage - GA N.81449), we are conducting the development of a Smart Active Multisensor for the detection of some environmental pollutants and their morphological and chemical-physical characterization is being carried out in parallel with sensitivity tests.
An easy and cheap monitoring of the environmental museum condition is usually achieved using coupons that work as long-term passive monitors to reveal the possible surrounding pollution. Coupons can be made of different materials, sometimes the same of those composing the art objects of the collection in study. Metal coupons grant a fast-response and allow an easy trace back of the most dangerous indoor pollutants like, for instance, volatile organic compounds, because of the role they play on metal oxidation [1][2]. Within the PhD project AMAART (Active and Monitoring MAterials for the environmentally safe storage and exhibition of works of Art), conducted in parallel with the H2020 Project APACHE, metal film coupons in lieu of standard metal coupons were designed to reduce the time requested for a response thanks to their higher surface area and reactivity to pollutants [3]. The coupons were produced by metal sputtering and tested in various polluted environment to study their sensitivity and corrosion products depending on the time of exposure.
As regards the mitigation of pollutants' concentration, a study of the materials with high absorption capacity towards the selected pollutants was carried out and ceramic foam were chosen as porous substrate to be used as support of catalyst species suitable for the chemisorption of some organic volatile compounds.

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Design of mesoporous silica nanoparticles with high specific surface area and tunable size in the sub-micrometer regime

Federica Rizzi,[a,b] Rachele Castaldo,[c] Pierluigi Lasala,[a] Gennaro Gentile,[c] Marino Lavorgna,[d] Marinella Striccoli,[b] Roberto Comparelli,[b] Nicoletta Depalo,[b] M. Lucia Curri[a,b,*] and Elisabetta Fanizza[a,b]

[a] Department of Chemistry, University of Bari, Via Orabona 4, 70126 (Bari) Italy
[b] Institute for Institute for Chemical and Physical Processes, Italian National Research Council, Bari, c/o Department of Chemistry, University of Bari, Via Orabona 4, 70126 (Bari) Italy
[c] Institute for Polymers, Composites and Biomaterials, Italian National Research Council, Via Campi Flegrei 34, 80078 Pozzuoli (Naples) Italy
[d] Institute for Polymers, Composites and Biomaterials, Italian National Research Council, Piazzale E. Fermi 1, 80055 Portici (Naples) Italy

** presenting author*

Abstract

Mesoporous silica nanostructures (MSNs), synthesized by surfactant-directing approaches, attract high interest due to their unique physico-chemical features, such as large specific surface area and high pore volume, presenting a great potential in a variety of fields, including adsorption, catalysis and biomedicine. Even though size and shape can be tuned by tailoring reactant composition, reaction time and temperature, size tunability in the submicrometer (sub-µm) regime, crucial in many applications, remains challenging.

Here, two synthetic procedures are developed to achieve MSNs with size ranging from 30 up to 100 nm, using tetraethoxy silane (TEOS) as precursor in the presence of cetyltrimethylammonium bromide (CTAB) as surfactant and NaOH, as low cost base-catalyst, that advantageously leads to higher surface area MSNs. A reliable control on the reaction and growth steps and a successful modulation of MSNs in the sub-µm regime are attained by purposely balancing synthesis conditions, as TEOS and NaOH concentration, decreasing reaction temperature down to 30°C and tuning reaction time. The proposed comprehensive and in-depth systematic morphological and structural investigation enables a rational understanding of the mechanism and synthesis kinetic sustaining the regulation of MSNs size in such low dimensional regime, limiting the formation of micrometer sized MSNs, usually achieved from NaOH catalyzed-synthesis.

An Easy and Cost-Saving Approach to Synthesize Green-Emitting Carbon Dots from Cationic Surfactant Molecule

G. Minervini[a,b,c], M. Striccoli[c], E. Fanizza[b,c], A. Agostiano[b,c], M.L. Curri[b,c] and A. Panniello[c]*

[a] Polytechnic of Bari, Via Edoardo Orabona, 4, 70126 Bari, Italy; [b]University of Bari "Aldo Moro",Via Orabona 4, 70126 Bari, Italy; [c]CNR-IPCF-Bari Division, c/o Chemistry Department, University of Bari "Aldo Moro", Via Orabona 4, 70126 Bari, Italy

Carbon dots (CDs) are photoluminescent nanoparticles that have emerged in the last few years as greener and cost saving alternatives to semiconductor quantum dots and other heavy metal-containing luminescent compounds [1]. Their carbon-based chemical composition and the promising photoluminescence properties are making them progressively attractive for many fields of application.

Recently, a surfactant molecule, namely cetylpyridinium chloride (CPC), has been proposed as precursor for CDs [2]. In particular, exploiting the particular chemical structure of such precursor, CDs displaying a broad emission band in the green region of the visible spectrum can be simply prepared in a reaction with NaOH in mild conditions [2, 3]. Motivated by the energy and cost-effectiveness of such synthetic method, we explored new synthetic practices aimed to achieve an even easier and faster production of CDs with this approach.

We prepared CDs varying reaction conditions such as the precursor-to-NaOH concentration ratio, reaction temperature and time and we thoroughly characterized the resulting CDs optically and morphologically. All such parameters could be used as tools to regulate the kinetics of the process that converts the CPC into the green-emitting CDs, while the morphological and optical properties of the CDs are preserved. In particular, we highlighted that the reaction temperature is a crucial to enable a fast production of CDs. Indeed, the complete carbonization of CPC requires a very long time (from tens of hours to days [3]) if the reaction is performed simply at room temperature. On the other hand, under a mild heating of the reaction vessel at 70°C, the same result could be obtained in only tens of minutes.

Finally, we gave specific attention to the isolation and purification of the final products, and to the identification of intermediate species, contributing to the overall emission of the CDs samples [4]. In particular, we recognized that 2-pyridone molecular fluorophores are formed in the first steps of the reaction of CPC molecules with NaOH; then, such molecular intermediates are consumed as the reaction proceeds to form the green-emitting CDs. Our study advances both the knowledge on the mechanisms underlying the CDs formation in this particular synthetic strategy, and extends the set of synthetic tools to produce CDs in a such cost-effective and sustainable way.

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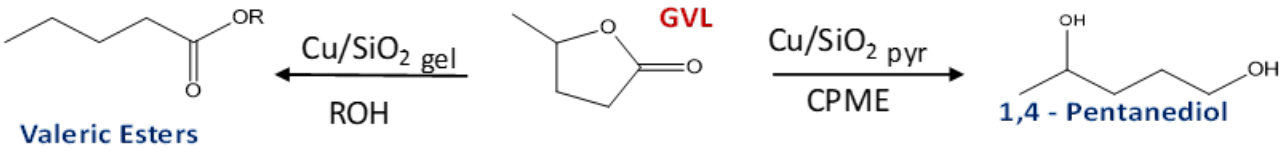
Catalysis and Green Deal

Nicoletta Ravasio

CNR-Istituto di Scienzze e Tecnologie Chimiche "G. Natta", via C. Golgi 19, 20133 Milano

Catalysis will play a pivotal role in the ecological transition, just as it does in the chemical industry nowaday. New processes are needed for the production of H_2, new fuels and bioproducts while keeping, whenever possible, a circular economy approach.
Cu catalysts have already proved to be valuable tools for the production of several Biobased chemicals. Selective hydrogenation of vegetable oils or of their methylesters in the presence of low loading Cu/Silica is very useful to improve their oxidative stability, a major barrier for their use in biodiesel and biolubricant formulations.[1]
The presence of Lewis acid sites on the surface of the same catalysts allows to set up bifunctional processes, as in the case of the one pot synthesis of valerate esters starting from γ-valerolactone (GVL) readily obtained from cellulosic biomass.[2] However, the number and strenghth of acidic sites can be finely tuned in order to reach high yield in 1,4 PDO that could be the monomer of new renewable- or semi-renewable polyurethanes and polyesters with improved properties. The hydrophilic/hydrophobic features of the silica support also played a role in addressing activity and selectivity



Hydrogen can be effectively produced over Cu/Al_2O_3 from secondary alcohols in the presence of an acceptor or a separation device.[3] This dehydrogenation reaction can also be used to produce bio-amines from bio-alcohols through the hydrogen borrowing technique. Finally the ability of Cu/SiO_2 to cleave β-1,4-glycosidic bonds can be successfully exploited for the valorization of lactose, a by-product of the dairy industry.[4]

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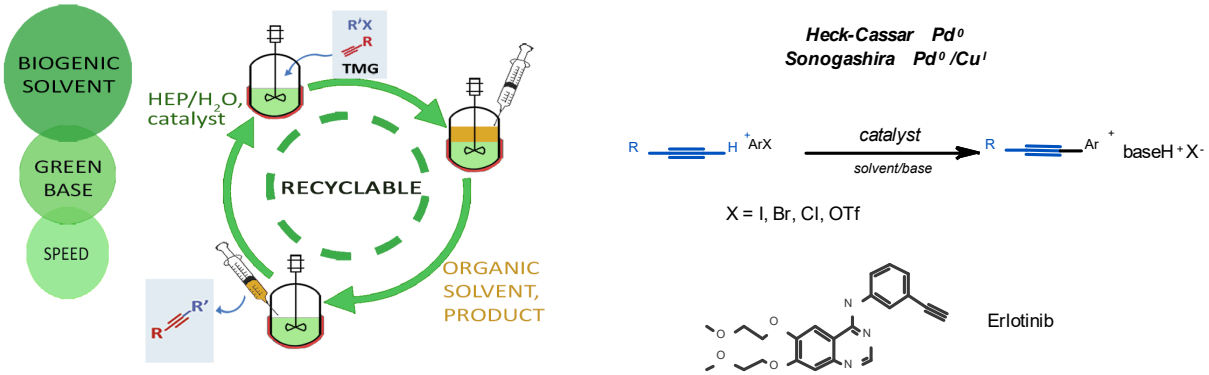
The Twelve Principles of Green Chemistry Translation Guide for Palladium Catalyzed Cross Coupling Reactions for Active Pharmaceutical Ingredients Sustainable Productions"

Walter Cabri,[a] Tommaso Fantoni,[a] Giulia Martelli,[a] Sara Bernardoni,[a] Lucia Ferrazzano,[a] Dario Corbisiero,[a] Paolo Cantelmi,[a] Federica Vacondio,[b] Francesca Ferlenghi,[b] Marco Mor,[b] Antonio Ricci,[c] Alessandra Tolomelli[a]

[a] P4i Lab, Department of Chemistry "Alma Mater Studiorum-University of Bologna, via Selmi 2, 40136-Bologna Italy; [b] Department of Food and Drug Sciences, University of Parma, Parco Area delle Scienze 27/a, 43124-Parma (Italy); [c]I&D, Fresenius kabi iPsum, via San Leonardo 23, 45010 Villadose (RO) (Italy)

Catalysis is one of the main alternatives to classical stoichiometric chemistry for carbon-carbon bond formation at industrial level.[1] However, a modern approach cannot avoid the inclusion of green elements from the beginning of the process design. In 1998, Anastas and Wagner[2] translated what we can define "chemical common sense" into The Twelve Principles of Green Chemistry, with the main target to inspire the development of industrial chemical synthesis. In particular, the principles highlighted the main requirements for the development of safe, cheap and environmentally friendly methodologies, identifying reaction conditions, reagents, solvents, renewable natural source material and energy to define the green chemical space. [3] The most important cross coupling reactions found a fertile environment in the pharmaceutical segment and, among them, Palladium catalyzed reactions, mainly discovered in the seventies, are nowadays by far the most versatile ones.[3,4] The discussion will be centered on a translation guide for chemists interested in catalysis, in order to facilitate the development of methodologies for the pharmaceutical industry. In addition, we focused the attention on the Heck-Cassar-Sonogashira reaction and on the evolution of the synthesis of a key intermediate of the tyrosine kinase inhibitor erlotinib, as an example of the process that should be followed in greening an industrial synthesis.[5]



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From University to Industry: examples on how university-industry collaborations in catalysis can be effective and successful

Pierdomenico Biasi

[a] *Casale Sa, Via Giulio Pocobelli 6, 6900 Lugano, Switzerland. p.biasi@casale.ch*

Cultures and work are rapidly changing for both universities and companies. Companies are looking for partners that are flexible and can provide added value, with an eye on the openness in research. Universities are realizing that findings need to be exploited and the industrial partners are the one that can make it happen. Despite this there is still a number of factors that make the research not effective as wished.
The chart below shows that while universities and their industry partners have different missions, they also have complementary skillsets. Each brings something to the table for innovative discoveries. University researchers are good at finding difficult problems and having the freedom to pursue different solutions; companies are good at taking discoveries and developing them as reported in the Figure below (Fig. 1).

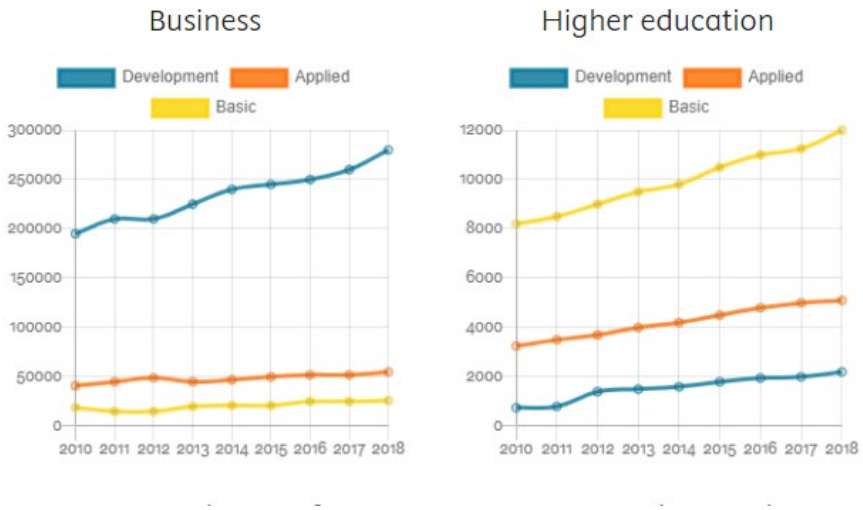

Figure 1: Source: NSF, USA National Patterns of R&D Resources: 2017-2018 Data Update. Expenditure in millions $ [1].

Challenging research sometimes is not possible directly in industry since the skills required are not present or not fully developed.
Together with PSI, Casale worked on DeNO$_x$/DeN$_2$O catalysts to be used in stationary applications in the nitric acid process. To study the catalysts operando techniques and synchrotron experiments were used. Combining the skills of the Applied Catalysis and Spectroscopy group at PSI, the access to instruments not available in industrial laboratories and the industrial development capabilities of CASALE to use basic research to identify and solve customer needs, the university/industrial partners were able to foster new discoveries that could be applied directly in the improvement of the NO$_x$ and N$_2$O abatement in nitric process. The case study will show how the relationship, the flexibility and the pragmatic focus on results led to the success of the collaboration.

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Polymer Brush Technology: the True and the False in Grafting to Processes

Michele Laus

Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Universitá del Piemonte Orientale "A. Avogadro", Viale T. Michel 11, 15121 Alessandria, Italy

Surfaces and interfaces play a critical role in many applications and devices [1]. Tuning hydrophilicity and hydrophobicity, tribology, adhesion and lubrication as well as antifouling characteristics is a fundamental requirement for the successful exploitation of forefront technologies ranging from optoelectronics to sensors and coatings. Since their introduction by the seminal paper of Alexander, polymer brushes appeared a rational and direct tool to achieve surface control at the desired level. The structural versatility inherent in polymer chemistry, combined with the remarkable ease of integration of polymer brush technology into industrial production lines, has paved applied science avenues for this technology. A multitude of polymer brush architectures including homopolymers, gradient and block copolymers, polyelectrolytes, reversible and responding systems have been described featuring a variety of functions, being adaptable and reprogrammable surfaces the actual frontier. At the same time, many theoretical issues were addressed which led to important contributions to understanding the physics of polymer brushes.

Basically, there are two distinct approaches to the preparation of polymer brushes: grafting to and grafting from methods. The grafting from approach involves a polymerization starting from the substrate surface modified with functional groups able to initiate the polymerization reaction. Relatively high grafting densities are obtained together with limited control over the polymer composition and brush thickness. The grafting to approach involves a grafting reaction of a preformed functional polymer to the substrate surface. Although lower grafting densities are generally obtained, the possibility of designing the polymeric architecture by controlled polymerization techniques and performing an accurate characterization before the grafting process allows a precise control over the brush structure and arrangement. Furthermore, since the grafting to reaction is a self-limiting reaction, a homogeneous and reproducible brush is expected to be obtained with enormous implications for proper integration of this technology into industrial production lines.

The self-limiting behavior is commonly ascribed to the entropic barrier generated by the pregrafted chains, which strongly reduces the probability of an unreacted chain to penetrate the brush and reach the substrate. In this contribution, the main characteristics of the grafting to reaction will be critically discussed and a new perspective will be provided for the mechanism [2]. In addition, novel effects concerning the molecular weight dependence of the grafting to, including peculiar partition mechanisms, will be described thus shedding new light into this fundamental process.

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CO_2 utilization: from waste to resource

Carlo Perego

[a] *Formerly SVP for the R&D Energy Transition and Biomass Program at Eni SpA.*

During the COP-21 in Paris in 2015, 195 countries have signed an agreement that provides for the implementation of all the necessary actions to contain the rise of the temperature below 2 °C compared to the pre-industrial era and, as a more ambitious target, to limit it within 1.5 °C. Climate change is strictly related to the increase of CO_2 concentration in the atmosphere. Last update (March 2021) by Global Monitoring Laboratory reported a CO_2 concentration of 416.34 ppm, with an average annual increase of 2.4 ppm in the last decade.
The International Energy Agency has recently published the "Net Zero by 2050" report, which define a roadmap to reach the net-zero CO_2 emissions (NZE) within 2050. [1]
This very ambitious target can only be pursued through the adoption of a series of actions aimed of reducing energy dependence on fossil sources, but also to valorize CO_2 with a circular economy approach. It means to transform waste CO_2 into products or services with a potential market value. The range of potential CO_2 applications is very large and it is part of the vast subject known as Carbon Capture Utilization and Storage (CCUS). This contribution will focus on a particular aspect of the utilization related to its transformation, by which CO_2 is chemically altered to produce useful products. Considering that, in order to positively contribute to the climate goals, the CO_2 utilization technologies must use low-carbon energy and displace products with higher life-cycle emissions, like building materials with permanent carbon retention.
Hence CO_2 will be regarded as building block for many different chemicals including energy vectors, polymers and chemicals, and inorganic carbonates. Among them, several groups have recently paid attention to the catalytic telomerization of CO_2 with butadiene. [2-6]
This reaction was the subject of pioneering research under the supervision of Prof. Paolo Chini since 1977. In particular the δ-lactone first reported by us in 1978 [7] has been considered as intermediate for the production of several chemicals originated by CO_2. [8-9]

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Benign by design strategies for a more sustainable future: the valorisation concept

Rafael Luque

[a] *Departamento de Quimica Organica, Universidad de Cordoba, Campus de Rabanales, Edificio Marie Curie, Ctra Nnal IV-A, Km 396, E14014, Cordoba, Spain; e-mail: rafael.luque@uco.es , tel: +34 957211050*

Producing, using, disposing…. The old-fashioned model still present in our society needs to give way to the concept of the circular economy in which Reducing, Reusing and Recycling are located at the core of all future endeavors in the productive model.

Going beyond the circular economy, the valorization concept aims to revolutionize the future of R&D in both academia and industry, producing wealth (valuable chemicals, materials, fuels, etc.) from waste and reducing, at the same time, environmental and socio-economic impacts of residues.

Based on the extensive experience of the applicant in the valorization concept, this contribution aims to provide an overview on the biomass/waste valorisation concept applied to success stories from lab research and discovery all the way to industrial examples.

Sustainability as Process Design Guidance for Flow and Plasma Chemistry

Volker Hessel

School of Chemical Engineering and Advanced Materials, University of Adelaide, Australia;
School of Engineering, University of Warwick, United Kingdom

Flow chemistry, process intensification, green chemistry, electrification of chemistry, and designer solvents are commonly seen as means of sustainable processing [1]. One has to be careful, however, with such generalized labelling, as any of those future technologies may lead to an environmental footprint worse than conventional technology [2]. It is much relevant that the emerging technologies really reveal their disruptive potential and the promise to industry, society and our planet is kept.

Seeing that, what actually hinders the full implementation? First of all, the flow chemist researcher is typically not trained in sustainability assessments; but admittedly, the use of simple green chemistry metrics is taken here and there. This is helpful as guidance for improving a reaction from a single point such as solvent or energy reduction, but does not reach the holistic view needed to address major issues of mankind such as global warming and clean water [2]. A second point which hinders a strong application of sustainability guidance is that flow chemists typically do not have insight in all the processes needed (including upstream, downstream-separation) and in processes 'at scale' (industrial production), as well as have a view beyond factory gate-to-factory gate (as opposed to cradle to grave/cradle; including supply chains, warehouses, transport) [2].

This presentation wants to show that, while sustainability assessment causes laborious extra work, it offers fascinating perspectives for the flow chemist and chemist in general [2]. Besides contribution to ecological matters, it can lead to better exposure of societal impact through research promotion (on social and classical media) and to the definition of business cases [3]. Finally, it can produce research of high innovation and quality, and change the way we are producing products and wealth.

This presentation will give a critical and holistic view about the sustainability of flow chemistry [3] and plasma processing [4], both considered as process intensification. Both simple and complex holistic tools for environmental quantitative assessment will be introduced. With the increasing complexity of assessment, green chemistry metrics [5], life cycle assessment methodology [6], and circular transition indicators [7] are discussed at selected examples and in a generalized manner. In this way, the sustainability is assessed first on the level of a reaction only, and then moving to a process level and beyond to a circular process much beyond the chemical factory. The presentation will show that extra-terrestrial (flow chemistry) processing [8], stimulated by the harsh conditions of the outer space (microgravity, possibly no Earth supply), can key give key learnings for chemistry on circularity [9], revisited from first principles and by posing "Unearth questions" [10].

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Waste-to-chemicals: a low-carbon innovative solution for circularity

Gaetano Iaquaniello[a] and Siglinda Perathoner[b]

[a] NextChem (Maire-Tecnimont group), Via di Vannina 88/94, 00156 Rome, Italy; [b] Dip. ChiBioFarAm - Univ. Messina,V.le F. Stagno D'Alcontres 31, Messina. Italy and European Research Institute of Catalysis (ERIC aisbl), Bruxelles, Belgium.

The implementation of a circular economy is a fundamental step to create a greater and more sustainable future for a better use of resources and energy. Wastes and in particular municipal solid waste represent an untapped source of carbon (and hydrogen) to produce a large range of chemicals from methane to alcohols (as methanol or ethanol), urea, hydrogen and others. Waste-to-chemicals (WtC) is an attractive alternative option, but still largely underestimated as a viable solution.

This lecture, which will be jointly presented by the two authors having received the Mario Giacomo Levi award from SCI (Division of Industrial Chemistry) for this activity, is briefly discussing the possibilities offered for a chemistry that starts from municipal waste and non-recyclable plastics and how this idea is entering a phase of industrial implementation, with Italian chemistry at the forefront in this direction in Europe. Depending on the configuration, carbon-negative technology can also be obtained on an LCA basis, and this represents one of the first examples of industrial technology with these characteristics.

The examples discussed regard the waste-to-urea, -hydrogen and -methanol processes. Results show that WtC technology is both economically valuable and environmentally advantageous (in terms of saving resources and limit carbon footprint) to produce chemicals from waste materials. Emphasis is given to the possibilities offered by this technology to provide novel solutions for energy-intensive-industries, from steel to chemical production and refineries. Some new advances such as the concepts of hybrids solutions with electrolysis to enhance carbon fixation or the production of ethylacetate will be also discussed. Finally, to remark the role and relevance of this solution in implementing alternative, and technologically ready, solutions to produce green H_2 as alternative to the more costly electrolysis method, will be also highlighted.

Forewords will be also shortly given to remember Mario Giacomo Levi role for industrial chemistry in Italy and his effort in the sustainable valorization of national resources of Italy.

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[3] E. Antonetti, G. Iaquaniello, A. Salladini, L. Spadaccini, S. Perathoner, G. Centi, *ChemSusChem* **2016**, *10*, 912.
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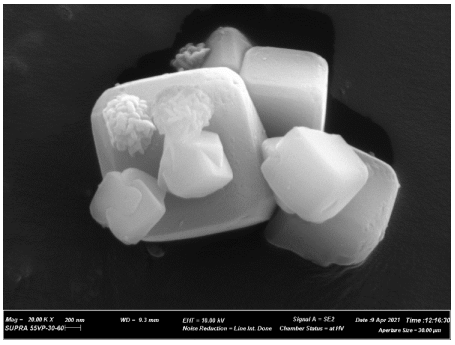
[9] Patent application. N. 102018000009364. Metodo ed apparato per produrre bio-metano da rifiuti, preferibilmente rifiuti industriali o urbani ed i loro derivati. Depositate date 11.10.18.

New generation of specialty zeolites for sustainable chemistry

Paolo Vacca[a], Miriam Riva[a], Marco Mudu[a], Katarzyna Fidecka[a], Wayne Daniell[b]

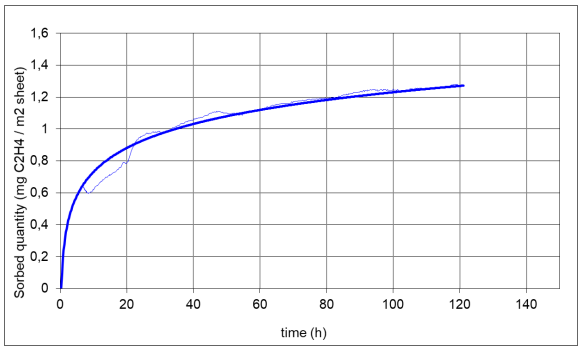
[a]SAES Group Research Labs – SAES Getters S.p.A., viale Italia 77, Lainate
[b]New Business Development, Specialty Chemicals Division, SAES Group

The continuous development of zeolite technology has opened up a myriad of applications for this important class of microporous aluminosilicate material in many fields of industrial, environmental and social relevance. Many different zeolite structures have been developed, encompassing a wide flexibility in terms of pore dimensions, channel geometry and chemical composition. Framed within this context is SAES' development activity, establishing a sustainable technology platform capable of breathing new life into the field of functional materials, and making specialty zeolites suitable for integration of new functionalities in a host of established products. In this paper, we will demonstrate the potential of our zeolites, not only through their functionality, but also according to their environmentally 'green' character, their non-toxicity and safe operation.



From the very beginning of this activity, we at SAES decided to make sustainability the core of our development process. We adopted a process design for the environment, where all development phases are submitted to an environmental impact evaluation, which excludes the use of any organic template. Zeolite preparation processing has been redesigned to limit the consumption of valuable resources, utilizing a green, sol-gel hydrothermal synthesis route enabling the production of nanozeolites shaped in different framework structures and compositions.

These materials offer unique and entirely different optical, mechanical and functional properties compared to conventional micro-size materials. In particular, their surface chemistry and internal volume properties can support new strategies for the integration of functional properties into industrial applications where SAES' Specialty Chemicals technology platform can play an important role [1-3].



Different examples will be discussed, including gas management, optical detection and biocidal applications. New specialty zeolites have been designed to capture ethylene in food packaging applications, being utilized in thin coating configuration where particle size control and surface properties are fundamental requirements for industrial adoption. Continuing the exploitation of zeolite characteristics, it will be shown how zeolite porosity can represent a suitable environment for hosting of active molecules. Finally, a recent development highlighting zeolites effective against SARS-CoV-2 virus activity will be presented. This new class of modified zeolite could represent a new frontier for adoption of functional materials with high social relevance.

[1] WO2012004222 [2] WO2017141159 - [3] WO2016125050

Solvent free selective oxidation of benzyl alcohol over supported Ru catalysts

Eleonora Aneggi[a], Filippo Campagnolo[b], Jacopo Segato[b], Daniele Zuccaccia[b], Walter Baratta[b], Jordi Llorca[c], Alessandro Trovarelli[a]

[a]Dipartimento Politecnico, Università di Udine; [b]Dipartimento DI4A, Università di Udine; [c]Institute of Energy Technologies, Universitat Politècnica de Catalunya

Selective oxidation reactions are among the most important reactions in industrial processes and in particular, the oxidation of alcohols to carbonyl compounds is one of the fundamental reactions in synthetic organic chemistry due to the wide use of these products as precursors and/or intermediates of numerous compounds such as drugs, vitamins and fragrances [1]. From an environmental point of view, it is necessary to develop new green procedures with innovative catalysts that are active and selective in the presence of molecular oxygen [2]. Here we have developed a high efficient Ru-based catalyst supported over ceria-zirconia solid solution which is very active in the solvent free selective oxidation of benzyl alcohol with molecular oxygen.

Three different high-surface area supports (ZrO_2, CeO_2 and $Ce_{0.8}Zr_{0.2}O_2$) doped with 2 wt.% Ru were investigated (named respectively Zr2Ru, Ce2Ru and CZ2Ru). XRD analysis exhibits the formation of ruthenium oxide, RuO_2 (signals at 2θ = 35,1°and 54,5°), in perfect agreement with preliminary XPS characterization. In addition, XPS revealed that Ru dispersion is remarkably stable for CZ2Ru. A complete selectivity was obtained for all investigated catalysts. Zr2Ru showed a very low activity with a maximum of 21% of conversion at 90 °C (Figure 1A). When ceria is used as support an increase to 29% was observed. CZ2Ru is the most active material with a remarkable conversion of 61% at 90 °C, resulting among the most active catalyst reported in literature in solvent free conditions. When the reaction was carried out in solvent (ethanol) at 80 °C, after 6h a 90% of conversion was achieved confirming the remarkable activity of the CZ2Ru catalyst. Reducibility of materials has also been investigated by H_2-temperature programmed reduction (Figure 1B). All the catalysts exhibit reduction peaks related to Ru species at low temperature <150 °C. For Zr2Ru only one peak is detected, due to the reduction of RuO_2, while for ceria-based materials, two distinguished sharp peaks are visible. These latter have been assigned to the reduction of RuO_2 with different strength of interaction with CeO_2-based support. The higher reducibility of CZ2Ru is correlated to the enhanced activity of the catalyst in benzyl alcohol oxidation compared to the other samples.

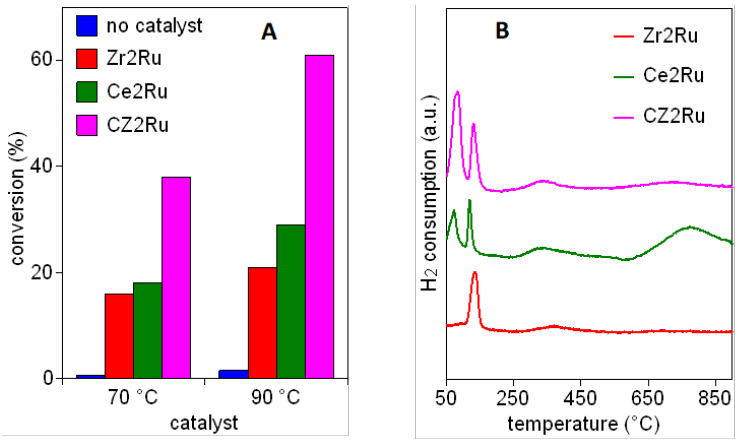


Figure 1. A. Benzyl alcohol conversion over Ru/catalyst (1 ml of benzyl alcohol, 200 mg of catalyst, 24 h, 10 mg of hexamethylbenzene as internal standard); **B.** temperature programmed reduction.

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The role of support wettability and acidity in the hydrogenation of γ-valerolactone over Cu/SiO_2 catalyst

Denise Cavuoto[a,b], *Nicoletta Ravasio*[b], *Nicola Scotti*[b], *Antonella Gervasini*[a], *Sebastiano Campisi*[a], *Marcello Marelli*[c], *Giuseppe Cappelletti*[a], *Federica Zaccheria**[b]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, via C.Golgi 19, 20133 Milano*
[b] *CNR – SCITEC "G.Natta", via C. Golgi 19, 20133 Milano*
[c] *CNR – SCITEC "G.Natta", via G. Fantoli 16/15, I-20138 Milano*
* *federica.zaccheria@scitec.cnr.it*

The scope of this abstract is to report that copper catalysts prepared by the Chemisorption Hydrolysis (CH) method[1] on moderately acidic support such as silica can effectively and selectively promote the hydrogenation of γ-valerolactone (GVL) to 1,4-pentanediol (1,4-PDO), a monomer of new renewable or semi-renewable polyurethanes and polyesters. GVL hydrogenation reaction yield to 1,4-PDO with Cu/SiO_2 system could be strongly driven by the choice of the silica support with different wettability and acidity properties. An unfavorable interaction of the 1,4-PDO product with the catalyst surface may lower the chance of secondary reactions. Moreover, the acidity of the catalyst could affect conversion and selectivity towards the 1,4-PDO product. Finally, these properties could also influence the copper dispersion at the surface of the catalyst.
Wettability properties of two commercial silicas SiO_2 A and SiO_2 B were evaluated through contact angle measurements and silanol density measurements. They showed that SiO_2 A has a less hydrophilic character with a lower hydroxyl density (3.1 $mmol_{OH}/g$ respect to 6.6 $mmol_{OH}/g$) and a higher contact angle (25° vs 19°). Moreover, *intrinsic* acidity titrations[2] in the solvent cyclohexane by phenyl ethylamine probe were carried out. They showed that SiO_2 B possesses a remarkable higher acidity (0.8 $m_{eq,PEA}/g$) compared to SiO_2 A (0.43 $m_{eq,PEA}/g$).
Subsequently, two copper catalysts were prepared utilizing the CH method as deposition method obtaining the CuO/SiO_2 A and CuO/SiO_2 B samples with a nominal copper loading of 16%. The catalysts were tested in the catalytic hydrogenation of GVL to 1,4-PDO. The results indicated that the choice of the support and solvent (dioxane and cyclopentyl methyl ether, CPME) has a pivotal role in increasing the reaction yield towards 1,4-PDO. The best results were achieved using the green solvent CPME and the catalyst CuO/SiO_2 A (78% yield of 1,4-PDO).
FT-IR spectra studies of pyridine adsorption on Cu/SiO_2 A and Cu/SiO_2 B exhibited the presence of only Lewis acidic sites on both the catalysts with a slightly higher amount on Cu/SiO_2 A with respect to Cu/SiO_2 B (0.18 $mmol_{py}/g_{cat}$ and 0.15 $mmol_{py}/g_{cat}$, respectively). A study of the *intrinsic* (in cyclohexane) and *effective* acidity (CPME and dioxane) showed that CuO/SiO_2 A has lower acidic sites in CPME compared to dioxane. A lower acidity under reaction conditions may account for the higher selectivity to 1,4-PDO observed in this solvent. Neither support showed any acidity in the CPME and dioxane solvents. Thus, in the reaction environment, catalysts could bear only a Lewis type acidity given by copper. XPS analyses showed that CuO/SiO_2 A possesses a higher surface copper concentration than CuO/SiO_2 B, considering both the calcined and reduced state. In the first case Cu/Si ratio is equal to 0.180 for CuO/SiO_2 A versus 0.046 for CuO/SiO_2 B. On the other hand, in the case of the reduced catalyst the ratio is 0.089 for CuO/SiO_2 A versus 0.026 for CuO/SiO_2 B. A higher Cu-surface concentration on SiO_2 A was associated with a higher hydrogenation activity.

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Improved Catalytic Transfer Hydrogenation of alkyl levulinates with alcohols over ZrO_2 based catalysts

T. Tabanelli[a], R. Bacchiocchi[a], E. Paone[b], P. Blair Vásquez[a], R. Pietropaolo[b], N. Dimitratos[a], F. Mauriello[b] and F. Cavani[a]

[a]Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale del Risorgimento 4, I-40136 Bologna, Italy; [b]Dipartimento DICEAM, Università Mediterranea di Reggio Calabria, Loc. Feo di Vito, I-89122 Reggio Calabria, Italy

Levulinic acid (LA) and its esters (LE) are polyfunctional molecules that can be obtained from lignocellulosic biomass. Because of LA peculiar structure and reactivity, the United States Department of Energy has classified it as one of the top 12 bio-building block chemicals. Nowadays, the most common strategy for its valorization is the chemical reduction in order to obtain valuable compounds such as fuel additives, solvents and intermediates. In particular, γ-valerolactone (GVL) has been proposed both as an innovative "green" solvent (due to its low toxicity, high stability and high boiling point) and as bio-based liquid fuel.[1] GVL may be obtained from LA by catalytic transfer hydrogenation (CTH) through the Meerwein-Ponndorf-Verley (MPV) mechanism. This approach uses organic molecules (e.g. alcohols) as reducing agents for substrates which contain a carbonyl group. Most of the studies published for the CTH of LA and its esters have been performed in liquid phase using batch reactors and ZrO_2 as heterogeneous catalyst.[2] However, high autogenic pressures are needed in order to work in the liquid phase at high temperature with light alcohols. Moreover, the CTH of alkyl levulinates using methanol or ethanol as solvents/H-donor were found to be inefficient in GVL production in the traditional liquid phase conditions. Better results can be obtained by using isopropanol in good agreement with the greater tendency of secondary alcohols to release hydrogen. For all these reasons, we decided to synthesize different high-surface-area ZrO_2 (both tetragonal "t" and monoclinic "m") and test their catalytic activity for the gas-phase continuous-flow production of GVL through CTH of LE. In this way, by working at 250°C with a contact time of one second over t-ZrO_2, LE can be completely converted promoting the formation of GVL with good to excellent yield of 68% and 80% when ethanol or 2-PrOH are used as reducing agents respectively. [3] For the sake of comparison, under batch conditions the CTH of LE using isopropanol leads to a comparable GVL yield only after 24h at 250°C.[4] Unfortunately, ZrO_2 undergoes to a progressive deactivation during the time-on-stream, due to the deposition of heavy carbonaceous compounds over the Lewis acid sites. However, a complete regeneration of the catalyst can be promoted *in-situ*, in the same reactor, by feeding air at 400°C. These results represent the very first examples of the CTH of LE under continuous gas-flow conditions ever reported in literature and the interesting reactivity showed with ethanol may open new perspectives in using bio-ethanol as reducing agent for the upgrading of bio-based platform chemicals. Finally, the effect of the zirconia phases (monoclinic and tetragonal respectively) on the catalytic activity has been further investigated and new efforts are directed toward the synthesis of zirconia mixed metal oxides (e.g. Ti-doped zirconia) with the aim of promoting the catalytic activity and stability for the gas-phase continuous flow production of GVL.

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Reconstruction phenomena in a Pt/γ-Al_2O_3 catalyst under hydrogenation conditions

E. Vottero[a], M. Carosso[a], M. Jimenez Ruiz[b], C. Chizallet[c], P. Raybaud[c], M. Manzoli[a], S. Morandi[a], R. Pellegrini[d], E. Groppo[a], and A. Piovano[b]*

*a) Department of Chemistry, NIS Centre and INSTM, University of Turin, Via Pietro Giuria 7, Turin, I-10125, Italy; b) Institut Laue-Langevin (ILL), 71 Avenue des Martyrs, 38042 Grenoble, France; c) IFP Énergies nouvelles, Rond-point de l'échangeur de Solaize, 69360 Solaize, France d) Chimet SpA–Catalyst Division, Via di Pescaiola 74, Viciomaggio Arezzo, I-52041, Italy *eleonora.vottero@unito.it*

The catalytic activity of supported platinum nanoparticles has been well known for a long time, but a complete understanding of the related phenomena at an atomic scale is still missing. In this work, we highlight the dynamics of the hydrogenated nanoparticles on a Pt/γ-Al_2O_3 catalyst under different H_2 partial pressures, obtained by a complementary use of FT-IR spectroscopy, Inelastic Neutron Scattering (INS) spectroscopy and Density Functional Theory (DFT) simulations. This work is part of a collaboration with the industrial partner Chimet S.p.A. (Arezzo, Italy).

Operando FT-IR was employed to follow the spectral evolution of the on-top Pt-H species linearly bonded to the nanoparticles (Figure 1A). In the presence of a N_2/H_2 flowing mixture (20 mL/min, 10% H_2) the signals of linear Pt-H species appeared (first plot). After H_2 removal (pure N_2 flux) the intensity of some of these bands unexpectedly increased before their complete disappearance (second plot) [1]. This behaviour was interpreted recurring to DFT simulations performed at IFPEN [2], which predicted a morphological reconstruction from a highly H-covered cuboctahedric structure, mostly featuring two-fold bridged Pt-H (not visible by FT-IR), to a biplanar structure mostly covered by linear Pt-H species (visible by FT-IR). The complementary information about the n-folded Pt-H species is obtained by means of INS spectroscopy, which provides vibrational spectra particularly sensible to all the H-containing species. The INS fingerprint for the Pt-H species measured under a high H_2 pressure of 420 mbar (Figure 1B, first plot) exhibits a remarkable similarity to the theoretical INS spectrum simulated for the cuboctahedric model optimised in [2], while the one collected at very low H_2 pressure (Figure 1B, second plot) is compatible with the simulated spectrum of the biplanar model. This second INS spectrum also shows the formation of a signal at 800 cm^{-1} compatible with -OH groups generated by H-spillover. Our set of data confirms the conversion for decreasing P(H_2) of bridged Pt-H species to linear ones (FT-IR) and the reconstruction of the Pt NPs from a cuboctahedric to a biplanar morphology (INS), as predicted by DFT.

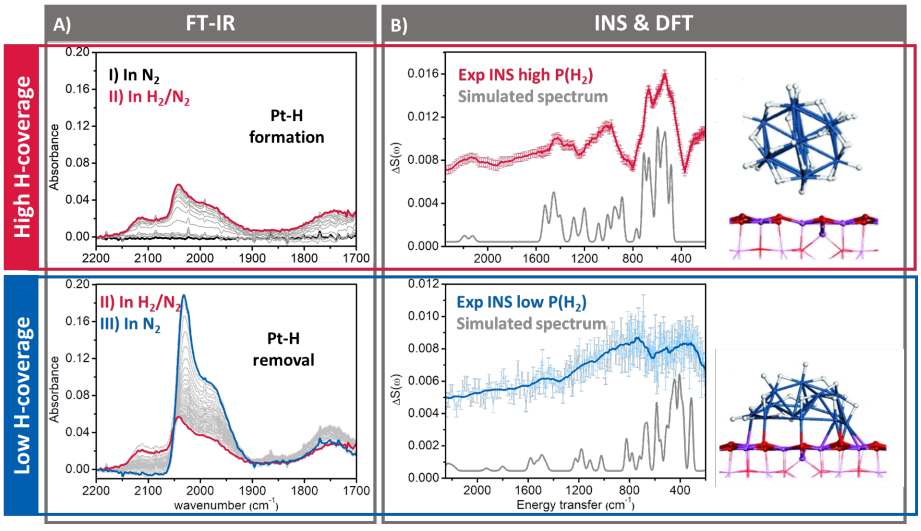

Figure 1: A) Evolution of the FT-IR spectra of linear Pt-H species in the presence of H_2 (red plot) and during its removal (blue plot). B) INS fingerprint of Pt-H species collected under a high H_2 pressure, compared with the theoretical spectrum of the cuboctahedric $Pt_{13}H_{32}$ cluster (red plot), and of the one collected at very low H_2 pressure compared with the simulated spectrum of the biplanar $Pt_{13}H_{16}$ model (blue plot).

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Structural Evolution and Enhanced Steam Deactivation Resistance of PtPd/CeO_2 Methane Oxidation Catalysts Prepared by Dry Milling

M. Danielis,[a] A. Mussio,[a] N. J. Divins,[b] J. Llorca,[b] S. Colussi,[a] A. Trovarelli[a]

[a]Dipartimento Politecnico, Università di Udine, and INSTM, via del Cotonificio 108, 33100 Udine, Italy; [b]Institute of Energy Technologies and Department of Chemical Engineering, Universitat Politècnica de Catalunya, EEBE, Eduard Maristany 10-14, 08019 Barcelona, Spain

The catalytic abatement of methane emitted from natural gas fueled vehicles (NGVs) presents some serious challenges for Pd-based catalysts which are commonly employed for this purpose. Primarily, the presence of 10-15vol% of water vapor in the exhausts deactivates the catalyst decreasing its activity [1]. In this respect, the addition of Pt to Pd-based catalysts has been found beneficial to improve their stability [2,3]. However, most recent studies were focused on the behavior of PdPt bimetallic nanoparticles [3] while the support effects were seldom considered.

Here, we report PtPd/CeO_2 catalysts prepared by a dry mechanical milling route which are not only stable during lean methane oxidation in presence of water, but also increase their initial activity during time-on-stream operation. Results show that bimetallic samples benefit from the recently reported peculiar structure of Pd/CeO_2 milled samples [4], in which Pd is spread all over ceria and partially embedded into the ceria lattice. In addition, both Pt and Pd species undergo a complex restructuring during operation, starting from the alloying of Pt and Pd and resulting in the formation of "mushroom-like" structures, as revealed by HRTEM analysis and summarized in Figure 1 [5]. This has been ascribed to the intimate contact between Pd and CeO_2 generated at nanoscale during the milling process; *in-situ* characterization techniques such as time-resolved XRD, near ambient pressure XPS and *in-situ* XAFS were used to follow their evolution during reaction.

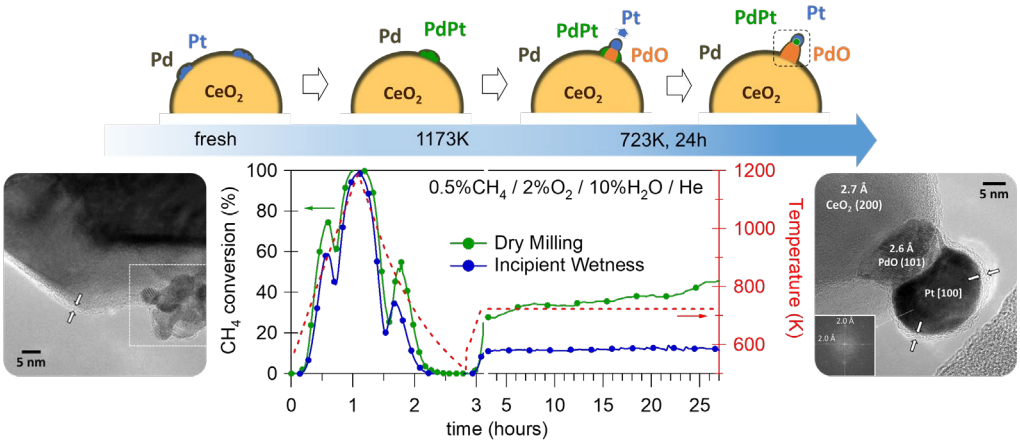

Figure 1. Scheme of PtPd reconstruction on ceria under methane oxidation tests (transient, up to 1173K, and stationary, at 723K for 24 hours) and measured catalytic activity; HRTEM images of PtPdCe M as prepared (left) and after exposure to steam (right).

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Effect of promoters on the performances of Ni-Al_2O_3 catalysts for CO_2 hydrogenation

Paola Riani[a,b], Elena Spennati[c], Guido Busca[b,c], Gabriella Garbarino[b,c]

[a] DCCI, University of Genova, Genova, Italy; [b] INSTM, UdR Genova, Genova, Italy, [c] DICCA, University of Genova, Genova, Italy

In the frame of efficient CO_2 utilization routes, new and efficient nanostructured catalysts represent a key-challenge to obtain active catalysts and tailored acid-base properties.
Ni-Al_2O_3 catalysts have been widely investigated and commercially developed for the methanation of CO_x prior to ammonia synthesis, but in the frame of Carbon Capture and Utilization technologies more performant and stable catalysts are required. Nickel is preferred to noble based catalysts for the low cost, wide availability and possibly for the robust nature. However, the choice of the support, of suitable promoters nature and loading are widely investigated at research and commercial level, also in relation to the exothermic nature of the Sabatier reaction and possible catalyst deactivation for sintering of the active phase or carbon deposition [1]. In the present work, we investigated the performances of Ni/Al_2O_3 based- catalysts [2] by looking to the proper Ni content and to the introduction of suitable promoters both in terms of nature and loading; i.e., lanthanum [3,4], silicon [2,4], calcium [5], vanadium [5] etc. The catalysts have been synthesized by different procedures and deeply characterised by XRD, FE-SEM, EDX, IR, DR-UV-vis-NIR, XPS, H_2-TPR and N_2 adsorption-desorption. As well, the determination of acid-base properties has been carried out by IR spectroscopy of probe molecules. Catalytic experiments were conducted in fixed bed flow reactors at atmospheric pressure with a total flow rate of 80 NmL/min and the following gas composition 6% CO_2, 30% H_2 and 64% N_2. Temperature has been varied in-between 523-773 K and product have been monitored by an online IR spectrometer. On best performing catalysts, experimental kinetics have been experimentally determined.
The addition of La strongly improves catalytic activity in CO_2 methanation at low temperature, the best methane yield (71%) arises at 573 K at 55000 h^{-1}, and over 14 La_2O_3 wt.% catalyst. This catalyst is completely selective to methane with no CO coproduction, as instead evidenced for the unpromoted catalysts. However, an increased loading points out changes in the structure of the support and consequently performances are reduced when compared to the best ones. The promoting effect of La- has been determined also when SiO_2 is introduced in the support even though, in this case, the active phase shows small presence of 2D NiO species due to the reduced interaction in-between nickel and alumina. Moreover, silica introduction (10 wt.%) completely hinders the interaction of lanthanum with alumina, preventing the formation of perovskite phases. This allowed to synthesize a catalyst achieving 86% yield to methane. The introduction of Ca and V improves catalytic performances in CO_2 hydrogenation [5]. In the present work, we will present how the support nature can affect the catalytic performances and as well, we will widely discuss it in relation to the surface chemistry of the synthesized catalysts.

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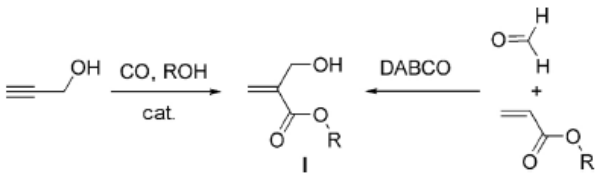
The alkoxycarbonylation of protected propargyl alcohols

Roberto Sole,[a] Alberto Scrivanti,[a] Matteo Bertoldini,[a] Valentina Beghetto[a], Md. Mahbubul Alam[b]

[a] Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca'Foscari Venezia, Via Torino 155, 40.
[b]Department of Chemistry, School of Physical Sciences, Shahjalal University of Science and Technology, Kumargaon, Sylhet, 3114, Bangladesh

Palladium-catalyzed alkoxycarbonylation of the C≡C triple bond of propargyl alcohol is a sustainable synthetic approach to 2-(hydroxymethyl)acrylates (**I** Scheme 1), a family of valuable intermediates which are usually obtained by Baylis-Hillman reaction.



Scheme 1. Alkoxycarbonylation of propargyl alcohol (left) *vs* Baylis-Hilmann synthesis of 2-(hydroxymethyl)acrylates (right).

As a matter of fact, esters of 2-(hydroxymethyl)acrylic acid are useful building blocks for the synthesis of natural products [1], biologically active compounds [2], and polymers. [3] Furthermore, acrylic esters such as are the immediate precursors from which enantiomeri- cally pure "Roche esters" can be obtained by asymmetric hydrogenation [4].
The developed synthetic protocol includes protection of the alcoholic function of the alkyne before its carbonylation in the presence of Drent's catalytic system.
Protection step effectively extends the catalyst life hence enhancing the practical applicability of the reaction. The effectiveness of some different protecting groups (benzyl, acetyl and trimethylsilyl) has been assessed and the influence of the reaction parameters investigated.
Acetyl groups demonstrated to very efficient protecting groups allowing for total TONs of up to 2000.
As far as the employed ligands, it appears that while PPh_2Py furnishes a little better TONs, the analogous PPh_2PyMe gives almost complete regioselectivity. We think that future improvements will be possible adopting other different ligands.

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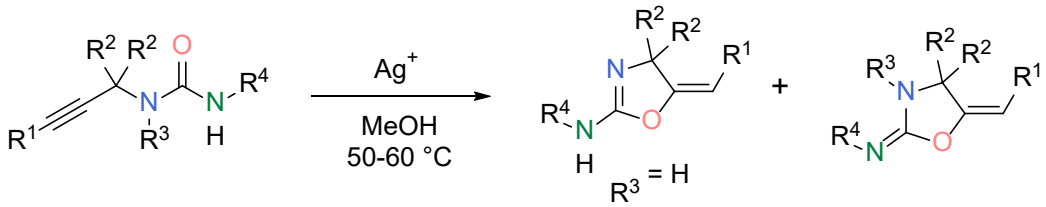
Unexpected *O*-5-*exo*-dig Cyclization of Propargyl Ureas to Oxazoline-2-amines Catalyzed by Silver Salts

Aleksandr Voronov,[a]* *Alessandra Casnati,*[a] *Paolo P. Mazzeo,*[b] *Alessia Bacchi,*[a,b] *Raffaella Mancuso,*[c] *Bartolo Gabriele,*[c] *Elena Motti,*[a] *and Nicola Della Ca'.*[a]

[a]*Department of Chemistry, Life Sciences and Environmental Sustainability (SCVSA) University of Parma, Parco Area delle Scienze, 17/A, 43124 Parma (Italy);*
[b]*Biopharmanet-tec, Parco delle Scienze, 27/A, 43124 Parma (Italy);*
[c]*Department of Chemistry and Chemical Technology, University of Calabria, Via P. Bucci 12/C, 87036 Arcavacata di Rende, Cosenza (Italy).*
**Correspondence: aleksandr.voronov@unipr.it.*

Recently our research group developed a superbase-catalyzed protocol to access imidazolidin-2-ones and imidazol-2-ones from propargyl ureas under ambient conditions[1]. A new silver-catalyzed *O*-5-*exo*-dig cyclization of ureas bearing an acetylenic moiety to oxazoline-2-amines is described. Good to excellent yields and the exclusive *E*-configuration of the external double bond have been achieved under mild conditions (50-60 °C). Previously known reactivity of silver would suggest the formation of imidazolidin-2-ones *via N*-5-*exo*-dig cyclization as for the case of basic catalysis[2], whereas the new catalytic system appears to favor the activation of *O*-cyclization pathway. To the best of our knowledge, it is the first example of the silver-catalyzed cycloisomerization of propargylic ureas leading to the formation of oxazoline derivatives. Alternative routes to oxazoline-2-amines are based on the palladium-catalyzed alkoxycarbonylation strategy[3,4] or non-catalytic methods providing low regio- and stereoselectivity[5].



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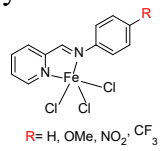
Kinetics of solketal synthesis promoted by Iron(III) complex

Francesco Taddeo [a], Vincenzo Russo [a], Roberto Esposito [a], Rosa Vitiello [a], Rosa Turco [a], Riccardo Tesser [a], Francesco Ruffo [a], Martino Di Serio [a]

[a] *University of Naples Federico II, Department of Chemical Sciences, Via Cintia, I-80126 Naples, Italy*

The growing interest in biofuels, mainly biodiesel, synthesized from the transesterification of vegetable oils has led to an increasing production of glycerol, obtained as by-product. Glycerol can be used for many applications, such as in cosmetics and food industries but it is not suitable for mixing with gasoline due to its high boiling point [1]. One of the most important reaction involving glycerol as raw material is the ketalization with acetone to obtain solketal. Ketals can be used as nontoxic solvents, fuel additives, plasticizers and suspending agents in pharmaceutical formulations [2]. The ketalization is a reversible acid-catalyzed reaction [2]. Among heterogeneous catalysts, solid acids such as Amberlyst, Zr- and Sn-mesoporous substituted silicates are used while homogeneous catalysts are both Brønsted and Lewis acids, such as *p*-toluenesulfonic acid or metal complexes. The advantages in using homogeneous catalysts are the high efficiency and the milder reaction conditions but they aren't easily separated from the product while the use of the heterogenous catalysts implies that the complete conversion of glycerol is rarely achieved [3]. Esposito et al. [2,3] investigated simple iron (III) complexes in the solketal synthesis showing their extraordinary efficiency with TOFs values up to 10^5 h^{-1}. In this work a kinetic study for the synthesis of solketal was performed in a batch reactor using an iron (III) complex as homogeneous catalyst with R=NO_2, reported in figure on the right. Experiments were made investigating different operative conditions (i.e. stirring rate, temperature and catalyst load).



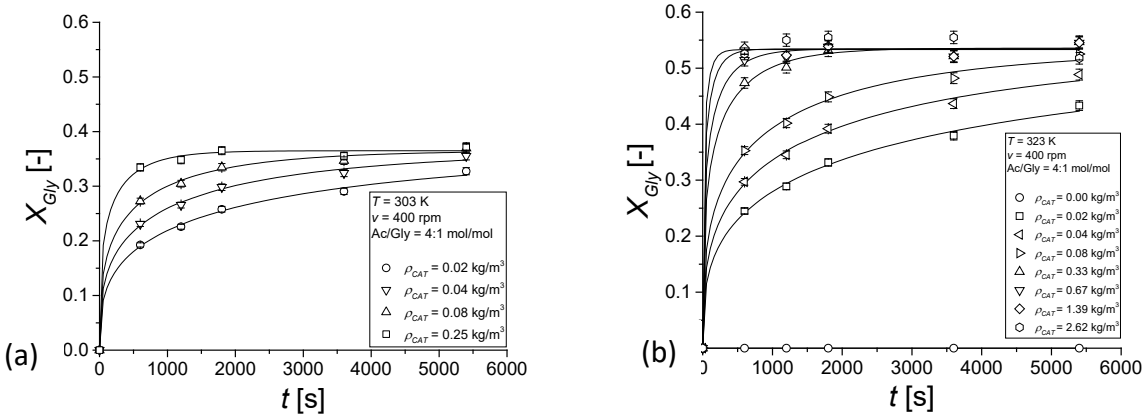


Figure 1: Catalyst load effect. Experiments performed at 400 rpm at T=303 K (a) and T=323 K (b).

The collected experimental data were interpreted with a mathematical model considering phenomena involved in the reaction network.

Acknowledgements

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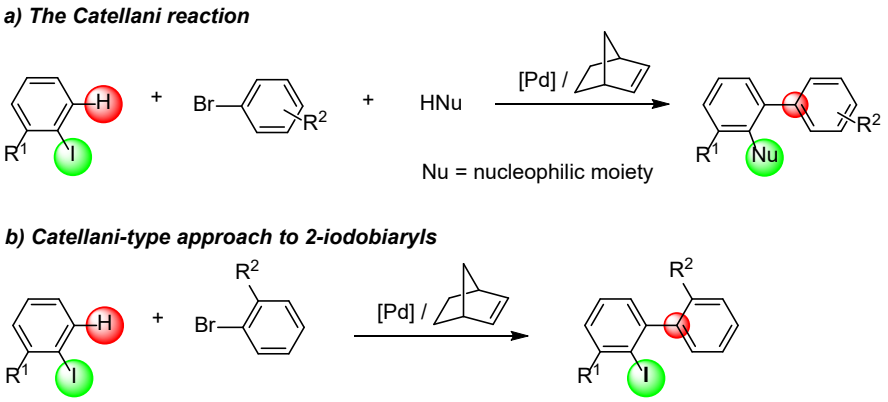
Palladium/Norbornene-Catalyzed Synthesis of 2-Iodobiaryls

Vinayak Botla, Elena Motti, Nicola Della Ca'

Department of Chemistry, Life Sciences and Environmental Sustainability (SCVSA), University of Parma, Parco Area delle Scienze, 17/A, 43124, Parma, Italy. e-mail: vinayak.botla@unipr.it

The biphenyl unit is ubiquitous in a series of high value-added organic compounds, such as pharmaceuticals, functional organic materials and natural products.[1] The biaryl scaffold can also be efficiently manipulated to prepare several classes of useful derivatives.[2] The costruction of biaryl scaffold can be achieved in environmentally friendly and step-economical way through C-H activation methodologies, including the Catellani reaction, which enables the construction of biaryl containing molecules with the cooperative action of palladium and norbornene (Scheme 1a).[3]
Here, we report a new direct approach to 2-iodobiaryl units based on the palladium/norbornene cooperative catalysis (Scheme 1b).



Scheme 1. Palladium/norbornene-catalyzed synthesis of 2-iodobiaryls.

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Heterogeneous catalysts for the liquid-phase degradation of simulants of organophosphorus chemical warfare agents

Stefano Econdi[a,b], *Matteo Guidotti*[b], *Stefano Marchesi*[c], *Simone Nascimbene*[c], *Fabio Carniato*[c] *and Chiara Bisio*[b,c]

[a]*Dept. of Chem., Univ. of Milan, Milan;* [b]*CNR-SCITEC, Milan;* [c]*DISTA, Univ. of East. Piedmont, Alessandria*

Chemical Warfare Agents (CWAs) represent a real danger for humankind. Typical countermeasures against these highly hazardous substances are based on detection tools, protection devices and conventional decontamination methods, such as dissolution, removal, destruction and combustion. Such methods need huge amounts of reactants and energy, and this poses several problems in terms of safety, environmental and economical sustainability, costs and disposal of the detoxified by-products. The main goal of the present research is the investigation and development of heterogeneous catalytic systems based on cheap and simple nanostructured materials for an effective, safe and sustainable degradation/decontamination of CWAs. As target substances, two organophosphorus compounds, paraoxon-ethyl and parathion-ethyl, widely used as pesticides in agriculture, were selected. They share a chemical structure akin to anti-cholinergic nerve CWAs, but with a significantly lower toxicity, thus representing valid simulants of these substances.

Paraoxon and parathion were dissolved in stock solutions at concentrations of 200 and 1000 ppm, in water or anhydrous ethyl acetate. The catalytic degradation tests were performed in batch glass reactors, under very mild conditions: room temperature and atmospheric pressure. The conversion of the organophosphorus substances was monitored by GC-FID, GC-MS, ^{31}P-NMR and HPLC, during a total reaction time of 24 h. The role of the controlled addition of H_2O and/or H_2O_2 was investigated as well. Two major classes of heterogeneous catalysts were considered: 1) synthetic saponite clays containing protonic (H-SAP), sodium (Na-SAP) or niobium centers (Nb-SAP) as well as in pillared form (P-SAP); and 2) commercial non-ordered mixed oxides 14.7% Al_2O_3-SiO_2, 1.4% TiO_2-SiO_2. The textural and morphological features of the fresh and the used catalysts were studied by N_2-adsorption and XRD techniques. Under anhydrous conditions in ethyl acetate, saponite-based solids showed a good activity in terms of conversion of paraoxon, up to ca. 80%. Over the commercial Al_2O_3-SiO_2 solid a maximum conversion of 92% was attained. The addition of H_2O_2, as an oxidant, did not lead to any improvement of the abatement capability. Under the tested condition, coupled with the results obtained from the experiments in water, it is assumed that hydrolytic and rearrangement processes, rather than oxidation ones, are the main factors governing the degradation of the organophosphorus species with these solids.

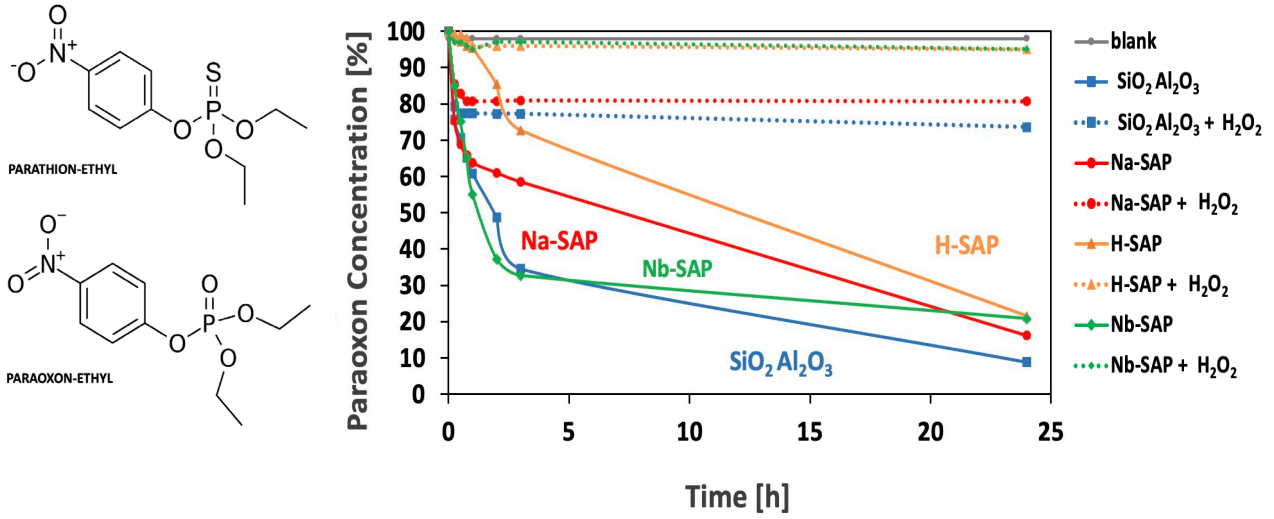

Figure 1. *Degradation conversion of paraoxon-ethyl over time in the presence (solid lines) and absence (dotted lines) of aq. H_2O_2 1% v/v (mol H_2O_2/mol paraoxon ratio 5:1). Reaction conditions: 1000 ppm paraoxon; AcOEt; 40 mg catalyst; 1 bar; 25 °C.*

Bio-oils valorization by selective catalytic hydrogenation: a comparison between batch and continuous flow systems

Annalisa Sacchetti[a], Tommaso Tabanelli[a], Maria Grazia Capraro[b], Luigi Capuzzi[b], Fabrizio Cavani[a]*

[a] *Dipartimento di Chimica Industriale "Toso Montanari", Alma Mater Studiorum- University of Bologna, Viale del Risorgimento 4, 40136, Bologna, Italy;*

[b] *NOVAMONT S.p.A, Via G. Fauser 8, 28100 Novara, IT*

**Corresponding author E-Mail: Annalisa.Sacchetti3@unibo.it*

Vegetable oils are considered both as suitable substitutes to traditional fossil fuels and chemical precursors to produce lubricant, monomers and additives, prompting the shift towards low impact and environmental-friendly bio refinery. Their importance is underlined by the rapid increase registered in oils production, raised of about 138% in 26 years[1]. One of the main strategies adopted for the valorization of bio-based fatty acids and triglycerides is the hydrogenation of the unsaturated fatty acids (UFA) with heterogeneous catalysts, which leads to the formation of the saturated (SFA) analogues. These are widely employed for the production of cosmetics, pharmaceuticals and for bio-based polymers applications[2]. Herein, the starting material supplied by Novamont S.p.A., which consisted of fatty acids solution derived from vegetable oils, underwent hydrogenation with the employment of commercial catalysts (noble metals supported on carbon) leading to promising results compared to what can be found in literature[2,3] . The main reaction parameters were optimize in a batch system and lead to complete conversion of UFA and Y_{SFA}=99% after 30 minutes with mild conditions (T=90°C,P_{H2}=4 bar) using Pd/C 0,3wt%. Finally, the same catalyst was also employed in a continuous flow system (H-Cube® Mini Plus), leading to complete conversion with τ=0,2 min (T=90°C, P_{H2}=20 bar) and strongly limiting catalyst deactivation issues (Figure 1). These results open new perspectives for a renovation in the scale-up of the continuous flow hydrogenation of UFA to SFA.

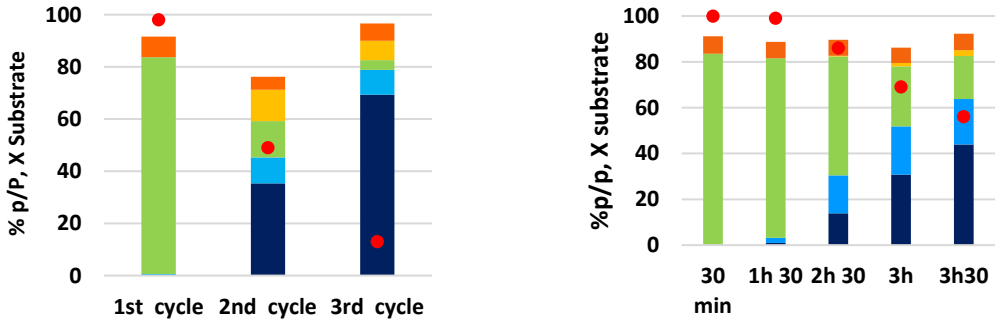

Figure 1: Stability test of Pd/C 0.3% wt ***Left*** batch (autoclave), ***Right***. H-Cube flow • Conversion ■UFA ■ SFA (*CIS*) ■SFA (*TRANS*) ■ shorter chain UFA ■ Poly-SFA

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Pd/CeO_2 as Passive NO_x Adsorbers: key properties and NO_x adsorption mechanism

Alessandra Toso, Sara Colussi, Alessandro Trovarelli

[a] *Dipartimento Politecnico e unità di ricerca INSTM Udine, Università di Udine, via del Cotonificio 108, 33100 Udine, Italy*

Passive NO_x adsorber (PNA) represent a promising technology to reduce NO_x emissions from vehicles during cold start periods and overcome the issues linked to poor efficiency at low temperature of SCR and LNT. A PNA should adsorb the NO_x emitted from the engine in the low temperature range, and release them when NO_x are converted efficiently in the SCR/LNT device, i.e. above 473 K. Among metal-oxide combinations, Pd on zeolites and Pd/CeO_2 materials showed good NO_x storage ability and appropriate desorption temperature [1,2]. In this work, several Pd/CeO_2 with different morphological properties have been prepared and NO_x adsorption capacity and desorption dynamics have been studied in correlation with their texture and morphology.

The results obtained by NO_x adsorption/desorption tests show that NO_x storage ability as well as NO_x storage efficiency of Pd/CeO_2 materials depend strictly on their surface area (Figure 1), whereas the morphology of the support and the Pd deposition method does not seem to play a key role. On the contrary, Pd deposition method controls the dynamics of NO_x desorption by affecting the amount of NO_x desorbed at different temperatures.

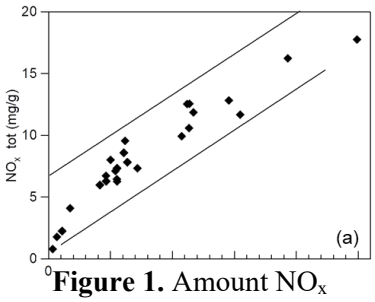

Figure 1. Amount NO_x stored against the surface area of Pd/CeO_2 materials.

The change in NO_x desorption efficiency might be attributed to the presence of active and stable Pd-O-Ce sites that promote the formation of the more stable nitrates, rather than nitrites. This seems to be corroborated by DRIFT measurements that correlate high NO_x desorption temperatures with the presence of nitrates while nitrites are predominant when low desorption temperatures are observed (Figure 2).

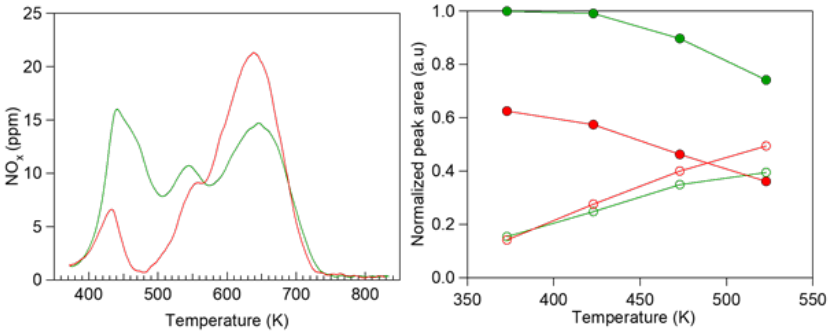

Figure 2. (a) NO_x desorption profiles on Pd/CeO_2 materials prepared by different methodologies: impregnation method (green), dry-milling (red); (b) evolution of nitrites (closed symbols) and nitrates (open symbols) on impregnated (green curves) and milled (red curves) sample with desorption temperature.

These findings highlight the key parameters to control the performance of Pd/CeO_2 materials for PNA applications. In particular, the results point out the possibility to control NO_x desorption efficiency by tuning properly the Pd-Ce interaction allowing the preparation of more efficient materials, with a NO_x desorption window close to the operating conditions of SCR device.

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A green route to the catalytic nitrous oxide decomposition by transition metal doped hydroxyapatites

Sebastiano Campisi,[a] Melissa G. Galloni,[a] Antonella. Gervasini[a]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, Via C.Golgi, 19, 20133, Milano, Italia;*

The development of eco-friendly and sustainable functional solid materials with remarkable catalytic performance in terms of activity, selectivity and stability is crucial for most of environmental catalysis processes. Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) - a bioavailable and biocompatible inorganic material - is at the centre of growing interest in heterogeneous catalysis, as it is known to be thermally and chemically stable and to possess a highly functionalized surface capable of anchoring active metal species [1]. Promising results have been recently reported over copper- and iron-functionalized hydroxyapatite catalysts in the selective catalytic reduction of NO_x (NH_3-SCR) and in selective catalytic oxidation of NH_3 (NH_3-SCO) [2-3].
In this work HAP powders modified with copper and iron species by a wet deposition procedure were tested in another reaction for air pollution control, namely the catalytic N_2O decomposition. Metal-loaded HAPs (with metal content ranging from 3 to 9 wt.%) were characterized as regards the texture (N_2 adsorption-desorption isotherms), phase composition (X-ray diffraction analyses), coordination of the transition metals (UV–vis diffuse reflectance spectroscopy), and surface composition and acidity (X-ray photoelectron spectroscopy and NH_3-titrations). All catalysts were then tested with respect to their N_2O decomposition activity in a lab-scale flow reaction line in 300-800°C interval (GHSV 30,000 h^{-1}), using a gas mixture of N_2O (150 ppm) and O_2 (6000 ppm).
Copper and iron-based catalysts were able to completely abate N_2O, although they showed some differences in the temperature window of activity (Fig.1, a). In general, the Cu-containing samples effectively operated at lower temperatures (T_{onset}= 350°C and T_{max}= 500°C) than those modified with iron (T_{onset}= 400°C and T_{max}= 650°C). To further assess the applicability of these systems under more realistic conditions, the time-on-stream stability as well as the resistance to sulphur and alkali poisoning were investigated. When tested at fixed temperature (550°C) and contact time (0.12 s), copper and iron catalysts initially lost about 10% of activity, then, after 72 h on stream, a constant value was maintained (Fig.1, b). An introduction of sulphur dioxide (50 ppm) into the reaction mixture slightly decreased the activity and shifted the temperature window to higher values (Fig. 1, c). Additionally, good resistance towards model poisoning with potassium and barium species was observed. Based on these results, metal modified hydroxyapatites emerge as promising active, stable and durable eco-friendly catalysts for N_2O decomposition reaction.

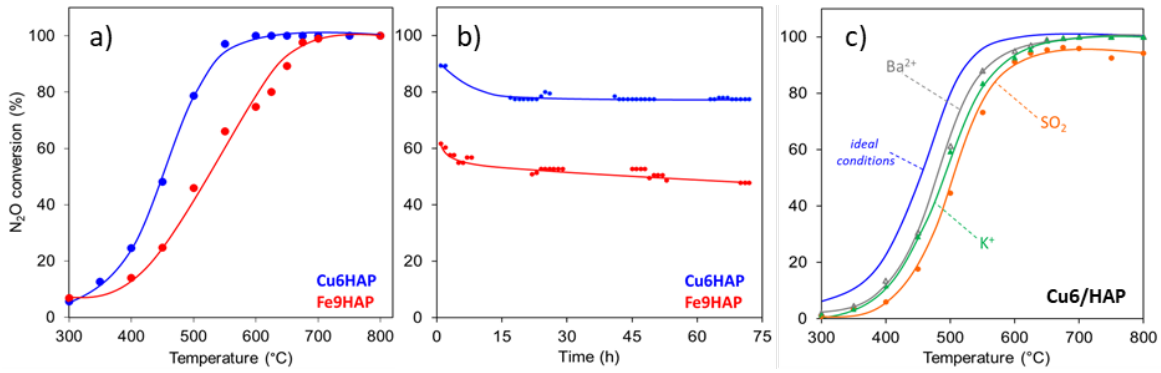

Fig.1: DeN_2O activity results: a) N_2O conversion (%) versus temperature over selected catalysts; b) Time-on-stream stability tests at T=550°C; c) results over Cu6/HAP in the presence of SO_2 in the gaseous feed and in Cu6/HAP sample poisoned with Ba^{2+} and K^+ species. Reaction conditions: [N_2O] =150 ppm, [O_2] =6000 ppm, contact time= 0.12 s.

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Ce doped WO_3-TiO_2 cordierite monoliths for Selective Catalytic Reduction of NO_x by NH_3

Consentino L.[1], *Migliore C.*[1], *Pantaleo G.*[1], *Liotta L.F.*[1]

1 – Institute for the Study of Nanostructured Materials (ISMN)-CNR, via Ugo La Malfa, 153, 90146, Palermo, Italy

The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia (NH_3) is the most efficient after-treatment technology for reducing NOx emissions from stationary and mobile sources [1]. Nitrogen oxides (NOx) are one of the major sources of air pollution and are responsible of a series of environmental problems such as acid rain, photochemical smog and the green-house effect [2]. The main commercial catalysts for the stationary source SCR process are V_2O_5-WO_3-TiO_2 [3]. Although such catalysts exhibited good activity at 300–420 °C, vanadium-based catalysts are still not satisfactory due to the narrow working temperature window, toxicity of V_2O_5 and low N_2 selectivity at high temperature [4]. In this perspective, many researchers are attempting to develop new environmentally friendly catalysts, without vanadium species, with the aim to apply to mobile sources. In recent years, CeO_2-based oxides have attracted increasing attention due to the excellent redox properties, oxygen storage capacity and non-toxicity [5].
In the present work cordierite honeycomb monoliths were washcoated with a CeO_2-WO_3-TiO_2 catalyst, characterized with several chemical physical techniques and investigated in NO SCR by NH_3 tests. A conventional home-prepared WO_3-V_2O_5-TiO_2 cordierite catalyst and a commercial reference were used for comparison. Hydrothermal aging treatments were performed, before NO SCR tests, in order to simulate long-term use in a diesel engine.

Acknowledgement. The project TECBIA "Tecnologie a Basso Impatto Ambientale per la produzione di energia sui mezzi navali" (Progetto n. F.090041/01/X36 –CUP B98I17000680008)" and the project PON ARS01_00334 – NAUSICA "NAvi efficienti tramite l'Utilizzo di Soluzioni tecnologiche Innovative e low CArbon" are acknowledged for financial support.

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The solar photothermo-catalytic approach for the VOCs degradation and the subsequent CO_2 conversion

R. Fiorenza[a], S. Scirè[a], M. Bellardita[b], L. Palmisano[b]*

[a] Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania; [b] Dipartimento di Ingegneria, Università di Palermo, ed. 6, Viale delle Scienze, 90128 Palermo)

Nowadays, high quality clean air for both indoor and outdoor environments is strongly recommended. New and green approaches such as the solar photocatalytic oxidation of volatile organic compounds (VOCs) can be considered suitable solutions for a sustainable air purification [1]. However, the products of the total oxidation of VOCs are water and CO_2. The carbon dioxide is considered the main greenhouse gas being emitted in large amounts from anthropogenic activities. Therefore, it is essential the development of new strategies that can mitigate the environmental impact of CO_2. In this contest, a hybrid catalytic approach, as the photothermo-catalysis, can be a fascinating route to obtain a high VOCs conversion at lower temperatures compared to the thermocatalytic combustion, with the possibility to further convert the produced CO_2 into value-added fuels (as CO, CH_4, CH_3OH, etc.) through the simultaneous action of heating and solar photoexcitation [2]. For this purpose, versatile (photo)catalysts are required, as mixed oxides able to show thermo and photo activities. In this work, we have synthesized brookite TiO_2-CeO_2 composites, to pair the photocatalytic features of the least common polymorph of TiO_2, with the thermocatalytic redox ones of CeO_2. The performance of the TiO_2-CeO_2 composite were evaluated in the photothermo combined approach, i.e. the toluene (model VOC) oxidation and the subsequent CO_2 conversion (**Fig. 1**).

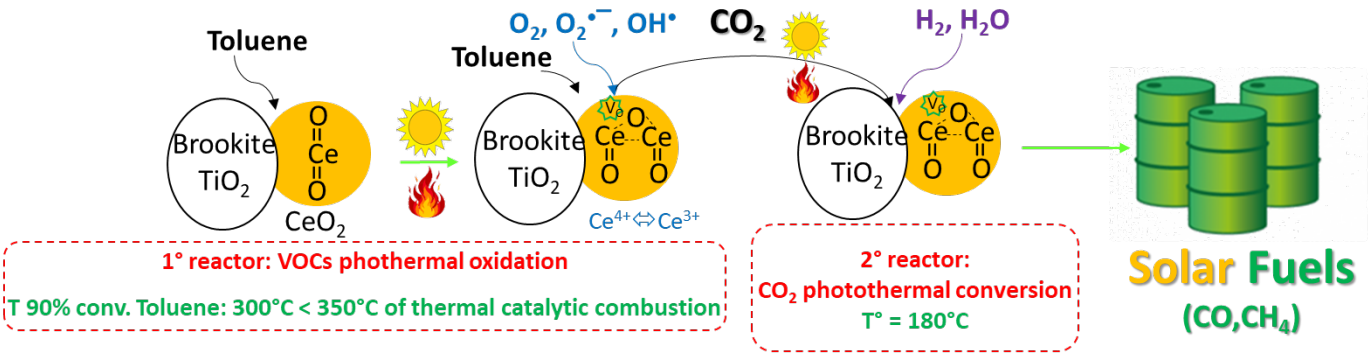

Fig. 1 *The proposed photothermo-catalytic combined approach for the VOCs removal and the following CO_2 conversion into solar fuels. V_o represents an oxygen vacancy.*

The characterization techniques (TEM, BET surface area, Raman, Photoluminescence, UV-vis DRS and XPS spectroscopies) pointed to the formation of an efficient heterojunction between TiO_2 and CeO_2, with a strong electronic interaction between the two oxides, facilitated by the peculiar features of brookite phase that favoured the formation of oxygen vacancies, boosting the redox properties of CeO_2, thus providing beneficial effects in both the reactions. The performance of the overall process can be tuned using two different catalysts in the reactors. Interestingly, the addition of a noble metal (Pd) on the TiO_2-CeO_2 improved the toluene mineralization whereas the simultaneous addition of small amounts of Co-Cu oxides on the same mixed oxide led to an efficient reduction of the obtained CO_2 into CO (mainly) and CH_4. This multi catalytic approach can be an effective strategy to obtain solar fuels starting from dangerous pollutants with a fascinating *VOCs to fuels* pathway.

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Cu, Fe, and CuFe exchanged hydroxyapatites as eco-friendly catalysts for NH_3-SCR reaction

M. G. Galloni,[a,b] S. Campisi,[a] W. Zhang,[b] A. Giroir-Fendler,[b] A. Gervasini[a]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, Via C.Golgi, 19, 20133, Milano, Italia;*
[b] *Univ. Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, 2 avenue A.Einstein, F-69622, Villeurbanne, France.*

Nitrogen oxides (NO_x) are common air pollutants with a harmful impact on the environment and human health. In the view of their abatement, the Selective Catalytic Reduction of NO_x by ammonia as reducing agent (NH_3-SCR) is the most valuable technology [1]. In this context, nowadays the ever more stringent criteria of sustainability and efficiency are moving researchers to find new, efficient, but at the same time low-cost, eco-friendly and robust catalysts.
For some years, our group has studied eco-friendly catalysts based on hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) [2] exchanged with Cu(II) and Fe(III) species for environmental reactions aimed at polluted stream denitrification. The developed materials showed satisfactory performances [3,4].
Herein, we present our more recent studies on monometallic (Cu or Fe) and bimetallic (CuFe, with equimolar Cu:Fe content) HAP samples with different metal loading (ca. 1-10 wt.%) obtained from nitrate precursors by wet-deposition procedure. N_2 physisorption, XRPD, UV-vis DRS, XPS, NH_3 adsorption experiments, and TEM-EDX provided fundamental details on morphological/structural properties with particular attention on metal speciation over the HAP surface. In particular, UV-DR and XP Spectroscopies revealed that the introduction of only 1-3 wt.% of Cu or Fe or (Cu+Fe) species on HAP assured good dispersion of metal phase, while increasing the amount of Cu or Fe (6-10 wt.%), some metal aggregates were also detected over the HAP surface.
The catalytic performances of Cu, Fe, CuFe samples in the NH_3-SCR reaction were explored in 200-500°C interval at fixed contact time (0.03 s) and evaluated also under real conditions (presence of 5% water in the gaseous feed). On some selected samples, stability and reusability tests were also performed in the absence/presence of water: the former at 400°C for 72 h, while the latter by repeating four successive cycles of reaction. All the samples were able to selectively convert NO_x to N_2 in the NH_3-SCR reaction. By way of example, Fig. 1 reports the profiles of NO_x conversion as a function of temperature for the bimetallic (CuFeHAP) sample and the monometallic (Cu and Fe) counterparts, loaded with ca. 6 wt.% of metal species. As a general trend, all the CuHAP and CuFeHAP samples resulted more active than Fe-based ones, independently on the metal loading. All the catalysts worked in 350-450°C interval with high selectivity to N_2 (ca. 90%) and a maximum NO conversion in 50-80% range in the absence of water. Conversely, a decrease of activity of ca. 30-40% was observed when water vapour was present in gaseous feed of gases.

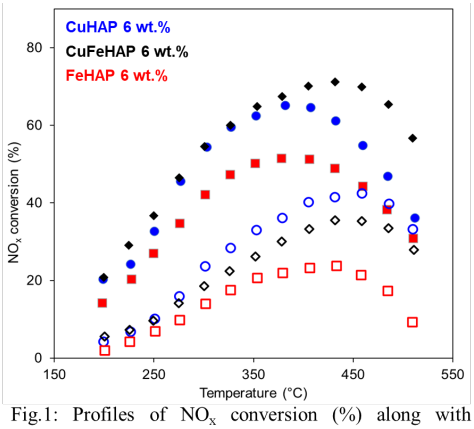

Fig.1: Profiles of NO_x conversion (%) along with temperature (°C) over Cu, Fe and CuFe HAP catalysts loaded with *ca.* 6 wt.% of metal species in the absence (full symbol) and presence of H_2O (open symbol). Reaction conditions: $[NH_3] = [NO] = 400$ ppm; $[O_2] = [H_2O$, if present$] = 5\%$; contact time = 0.03 s.

The obtained promising results move us to pursue on these activities, leading to new eco-friendly catalysts for reactions of air-quality protection.

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Photodegradation of Xenobiotics from Polluted Water Using a New PMMA-TiO_2 Based Nanocomposite

Fabiana Vento,[a] Angelo Nicosia,[a] Guido De Guidi,[a,d] and Placido G. Mineo[a,b,c]

[a] Department of Chemical Sciences and I.N.S.T.M. UdR of Catania, University of Catania, V.le A. Doria 6, I-95125 Catania, Italy; [b] Institute for Chemical and Physical Processes CNR-IPCF, Viale F. Stagno d'Alcontres 37, I-98158 Messina, Italy; [c] Institute of Polymers, Composites and Biomaterials CNR-IPCB; Via P. Gaifami 18, I-95126 Catania, Italy; [d] Centro di ricerca- Università di Catania "L'ora del mare"

Human activities affect the environment by introducing xenobiotics contaminants. This uncontrolled phenomenon leds to the need of efficient abatement systems. In this field, heterogeneous photocatalysis represents a promising technology for the removal of pollutants from air, surfaces and especially in water, by exploiting renewable energy sources [1][2].
Aeroxide® P25 titanium dioxide nanoparticles (TiO_2 NPs) stand out as one of the most efficient photocatalysts, usually employed in slurry form, despite their low ability in absorbing the Vis portion of the solar light radiation. Furthermore, subsequent removal of the suspended nanoparticles by expensive filtration procedures is required [3].
To cut costs and pave the way for commercial application, several approaches have been proposed to fix catalyst nanoparticles onto suitable supports [4]. A key solution could be immobilization of TiO_2 NPs onto polymer matrices, exploiting the polymer filmability to produce photoactive thin films. An easy way to embed TiO_2 NPs within a polymer matrix is to produce a PMMA/TiO_2 physical blend, despite the possible nanoparticles aggregation might be excluded. Poly(methyl methacrylate) (PMMA) represents an ideal candidate as support, due to its stability and transparency to visible light radiation.
In this communication, a new smart approach, involving the synthesis of nanocomposites through in situ bulk polymerization of Methyl Methacrylate with TiO_2 NPs, is proposed [5]. Their photocatalytic efficiencies under solar light irradiation were investigated by applying them as thin films in photodegradation experiments of Methylene Blue and Rhodamine B as model dyes and compared with homologues PMMA-TiO_2 NPs physical blend.
The nanocomposites photocatalytic activity was further applied for the abatement of xenobiotic pollutants such as acetaminophen (a drug) and paraquat (an herbicide).
The nanocomposites were characterized through Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), UV-Vis and Raman spectroscopies.
Experimental data revealed that the in-situ polymerization approach deeply influences the chemical-physical interactions between the polymer matrix and TiO_2 NPs, boosting the photocatalytic activity of the nanocomposite. Finally, a multi-faceted mechanism to explain the improved photocatalytic efficiency of the nanocomposites is also proposed.

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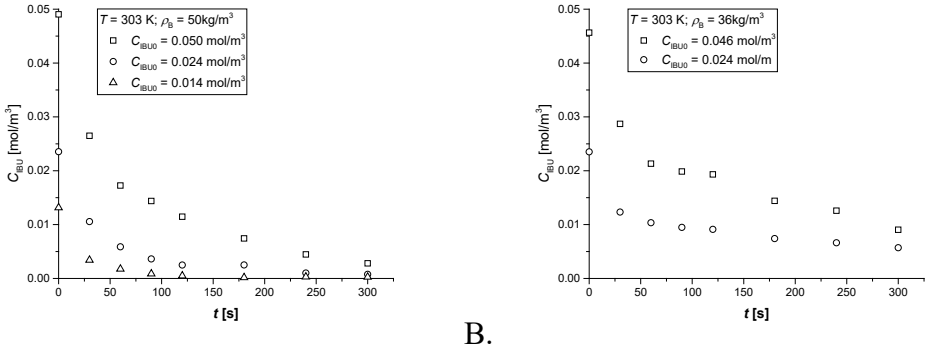
Heterogeneous photodegradation for the removal of ibuprofen from water

Vincenzo Russo, Maryam Hmoudah, Rosa Vitiello, Rosa Turco, Riccardo Tesser, Martino Di Serio

[a] *Department of Chemical Sciences, University of Naples Federico II, IT-80126 Naples*

The increase of Emerging Contaminants - ECs (which include pharmaceutically active compounds, personal care products, artificial sweeteners and endocrine disrupting chemicals) in wastewaters and the concern about the unknown long-term effects of their accumulation in the environment brought researchers to a growing awareness about the need to improve existing technologies and to develop new strategies for the removal of this new class of pollutants from wastewater [1]. Ibuprofen [2-(4-Isobutylphenyl) propionic acid] is a nonsteroidal anti-inflammatory drug (NSAID) that is primarily used as a painkiller and antipyretic. Due to its widespread use, it is one of the most prevalent ECs found in the environment, with detected levels in wastewater treatment plants influents which go from the tens to the hundreds µg/L [2].
Over the years, photodegradation was proved to be efficient method for wastewater treatment due to its high efficiency and low costs, also thanks to the employment of solid materials which can be easily separated and reused [3,4]: for this reason, this technology is promising for the removal of ECs from waters. The aim of this work is to conduct an in-depth study of the ibuprofen abatement processes through heterogeneous photodegradation, catalyzed by inorganic nanocrystalline semiconductors (commercial TiO_2 and synthetic CeO_2), to maximize the efficiency of these methods and to provide the kinetics for both processes.

Photodegradation experiments took place in a thermostatted, magnetically stirred 1.5 L glass jacketed reactor, in which air was bubbled through a mesh filter. Irradiation was provided through a UV lamp (365nm) inserted coaxially in the reactor. The experimental results showed that CeO_2 has an activity comparable with the commercial TiO_2 (Aeroxide P-25) in the photodegradation of ibuprofen. A higher conversion was obtained with higher catalyst concentration and temperature and lower initial concentration of ibuprofen (Figure 1).



A. B.

Figure 1 – Ibuprofen photo decomposition using: A. Aeroxide P-25 TiO_2, B. synthetic CeO_2.

As revealed, an increase of the decomposition rate is observed when increasing the initial concentration of ibuprofen for both catalysts, suggesting a first-order reaction rate.
Data was elaborated via rigorous kinetic models.

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Aquivion® PFSA-based spray-freeze dried composite materials for the conversion of furfuryl alcohol to levulinates

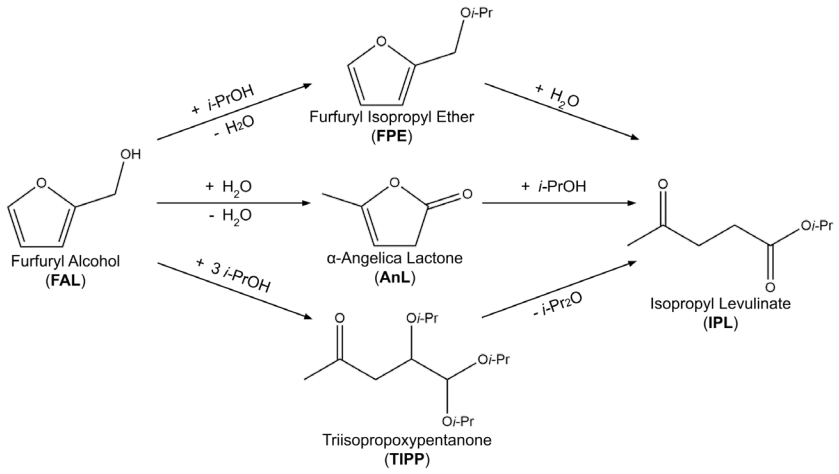
Alessandro Allegri[a], Manuel Bersani[a], Andrea Brigliadori[b], Ilaria Zanoni[b], Giuseppe Fornasari[a], Stefania Albonetti[a,b]

[a] Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy; [b] ISTEC-CNR, Institute of Science and Technology for Ceramics, National Research Council, Via Granarolo 64, Faenza, 48018, Italy.

Fluorinated acid polymers like Aquivion® PFSA have attracted interest from the scientific community in recent years for their unique and interesting properties, such as superacidity and high thermal and chemical resistances. Despite these most promising characteristics, its solubility, high cost and low accessibility of the acid sites are of hindrance in the direct application of Aquivion® PFSA as a catalyst.[1] The challenges that this material poses can be solved with the development of composite materials with an inorganic oxide via spray-freeze drying, a convenient and flexible technique.[2] In this work, it has been evaluated the possibility of preparing composite Aquivion® PFSA-based materials with different supporting oxides, such as silica, titania, and zirconia, and they have been tested in the conversion of biomass derived furfuryl alcohol to isopropyl levulinate, a promising platform molecule for the production of chemicals and fuels.

A range of innovative Aquivion® PFSA-based spray-freeze dried composite materials were prepared following the patented protocol,[2] varying both the nature and the amount of the oxidic phase therein contained. The oxides tested were commercial titania (Degussa P25), commercial silica (Ludox HS-40) and tetragonal zirconia synthesized following the procedure reported in literature.[3] The materials were characterized by means of SEM, TGA and BET, then tested as catalysts in the conversion of furfuryl alcohol to isopropyl levulinate in a 2-propanol solution.

All the samples displayed a significant, albeit different, activity in the studied reaction. Studying the produced species in the reaction mixture at different reaction times and temperatures by means of GC-MS provided insight on the different intermediates produced and the associated reaction pathways (Scheme 1), as well as the influence of the reaction conditions, especially the water content, on the outcome.



Scheme 1. Reaction pathway for the conversion of FAL to IPL.

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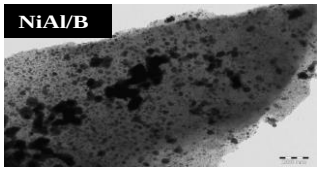
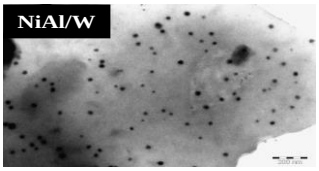
Biomass-derived levulinic acid hydrogenation to GVL using bifunctional biochar-based catalysts

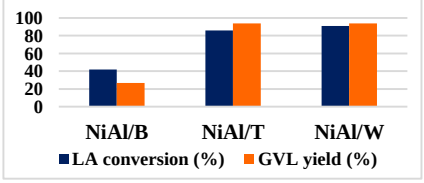
Somayeh Taghavi[a], Martina Tretti[a], Sebastiano Tieuli[a], Päivi Mäki-Arvela[b], Markus Peurla[c], Dmitry Yu. Murzin[b], Federica Menegazzo[a], Michela Signoretto[a]

[a] *CATMAT Lab, Department of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and INSTM Consortium, RU of Venice, Via Torino 155, 30172 Venezia Mestre, Italy*
[b] *Laboratory of Industrial Chemistry and Reaction Engineering, Faculty of Science and Engineering, Åbo Akademi University, 20520 Turku, Finland*
[c] *Faculty of Medicine, Institute of Biomedicine, Turku University, 20520 Turku, Finland*

The production of fuels and chemicals from renewable resources is a milestone and viable concept in the application of green chemistry. Gamma (γ)-valerolactone (GVL) with suitable physicochemical properties such as being a safe, biodegradable and nontoxic chemical and significant applications such as being used as a green solvent and fuel additive is considered as a value-added chemical in the recent years [1]. GVL can be produced from hydrogenation of levulinic acid (LA) which can itself be formed from acid catalyzed hydrolysis of biomass-derived cellulose or hemicellulose to their C6 and C5 mono-sugars and transformation of mono-sugars by passing through chemically active intermediates. LA to GVL reaction pathway follows tandem dehydration and hydrogenation steps or vice versa. The dehydration step requires a Lewis acid site and the hydrogenation step occurs in the presence of an active metal site [2]. Development of a cheap, green and suitable heterogeneous catalyst for the reaction is a precious topic for biorefineries and circular bio-economy [3]. In the present work, activated carbons derived from biomasses (activated biochars) were selected as novel supports for related reaction. In particular, activated biochars obtained from pyrolysis and activation of three different biomasses including vine wood waste (W), barley waste (B) and tannery shaving waste (T) were compared for their physicochemical properties using different characterization techniques such as N_2-physisorption, FTIR, TPD, and elemental analysis. Alumina as the Lewis acid site and Ni as non-noble metal active phase were precipitated and impregnated on the support, respectively and the obtained catalysts were named NiAl/W, NiAl/B and NiAl/T. Afterward, the catalysts performances were compared in the LA to GVL reaction. The reaction was carried out in an autoclave, using water as solvent in 30 bar H_2 at 200 °C for 4h. B with low surface area, low porous structure and lower carbon content caused the sintering of Ni metal particles (according to TEM image below) and low activity of the obtained catalyst in the reaction. On the other hand, W and T with higher surface area, suitable pore structure, higher carbon content caused better Ni particles dispersion and narrower Ni particle size distributions as were found in the TEM image. In addition, precipitated alumina in these two supports (W and T) with higher surface area led to the higher accessibility of acid sites and more acidity improvement according to NH_3-TPD analysis. All these significant properties led to the high performance of NiAl/W and NiAl/T with more than 80% LA conversion and more than 90% GVL yield.







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Aqueous phase reforming of biorefinery by-products towards sustainable hydrogen production

Giuseppe Pipitone [a], Giulia Zoppi [a], Samir Bensaid [a], Raffaele Pirone [a]

[a] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Turin, Italy,

Wastewater is of general concern for environmental sustainability. At the industrial level, carbon-laden aqueous streams must be treated and should be valorized to reduce environmental and economic concerns (e.g. in the food sector). This is similarly true for the developing biorefineries. Lignocellulosic biomass processing (such as pyrolysis, hydrothermal liquefaction, Fischer-Tropsch) results in secondary aqueous streams in which a high fraction of the initial carbon content of the biomass is virtually lost. Even the biodiesel production suffers from the same issue, since glycerol production excesses not the market needs. In this work, aqueous phase reforming (APR) has been proposed as a mild-temperature process able to convert oxygenated molecules present in the wastewater into a hydrogen-rich gas mixture [1]. A systematic study was carried out on the possible industrial scenarios of this technology looking both at synthetic and actual mixtures. Aim of the work was identifying the most suitable streams for APR in the possible industrial scale, pointing out the actual limitations and challenges faced for its development from the actual laboratory scale.

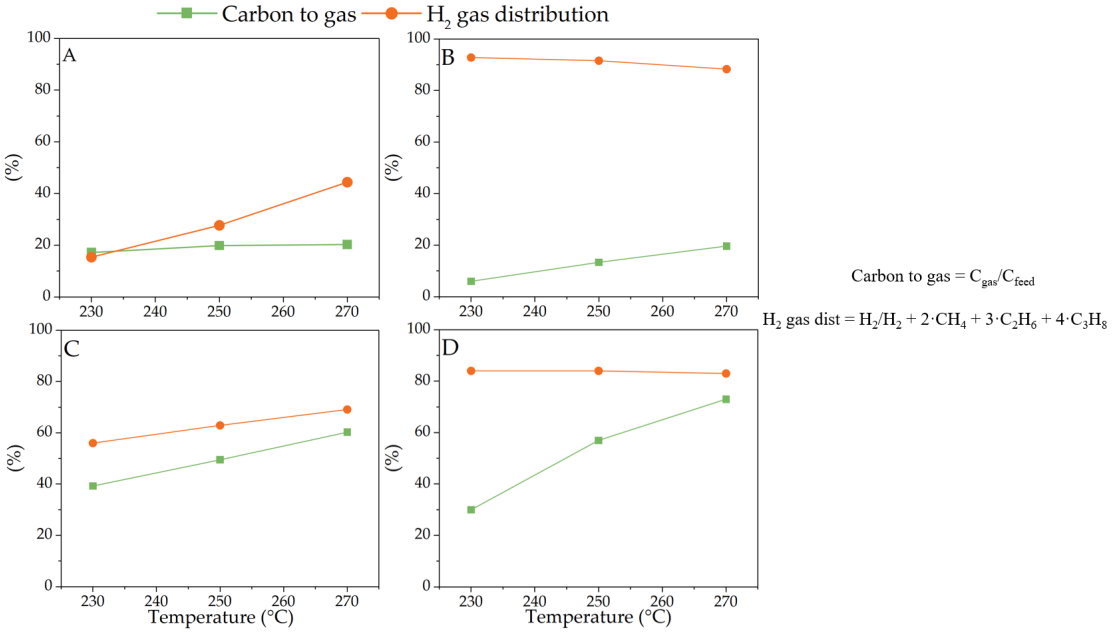

Figure 1. Influence of reaction temperature on APR of different substrates. A: wheat straw hydrolysate; B: synthetic mixture of water fraction from lignin-rich HTL; C: water fraction from Fischer-Tropsch; D: glycerol solution.

In Figure 1 some results from the experimental campaign are depicted. It can be observed that the influence of temperature is different according to the type of feedstock. Increasing the temperature favored the hydrogen distribution (i.e. the hydrogen production compared to alkane production) in the case of wheat straw hydrolysate and Fischer-Tropsch, while it was almost constant for the aqueous phase post HTL and for glycerol solution. The carbon conversion to gas was positively influenced in each case apart from the first one, where it remained constant. Apart from activity and selectivity, also the catalyst stability was evaluated in each of these scenarios, pointing out possible strategies to mitigate these issues. Moreover, the coupling of APR with other processes (e.g. HTL biocrude upgrading or green diesel production) were proposed.

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1,3-Dioxolan-4-Ones as powerful tool for the synthesis of functionalized PLA-based materials with tailored properties

Stefano Gazzotti,[a, b] *Hermes Farina*,[a, b] *Marco Aldo Ortenzi*,[a, b] *Alessandra Silvani*[a, b]

[a]*Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy. – Email: stefano.gazzotti@unimi.it*
[b]*CRC Materiali Polimerici "LaMPo", Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy.*

Within the pursue of environmentally friendly alternatives to oil-derived plastics, polylactic acid (PLA) has emerged as one of the best candidates, thanks to a winning combination of green nature and good processability properties. In addition, PLA is biocompatible and its degradation byproducts are harmless in vivo. On the other side of the coin, however, drawbacks such as poor toughness and poor thermal stability strongly limit its industrial applicability. For this reason, PLA-related research is usually aimed at improving its lacking properties, while preserving its good features. Compared to other strategies, the synthesis of highly functionalized PLA-based materials, endowed with tailored properties, is scarcely investigated, due to a reduced monomer scope. On a general level, when targeting modified PLA-based materials, functionalized α-hydroxy acids are usually easily accessible. However, direct polymerization of lactic acid and α-hydroxy acids in general is scarcely efficient. For this reason, on an industrial level lactide (i.e. the cyclic dimer of lactic acid) is employed, but the synthesis of modified lactides is extremely difficult to achieve, despite being extensively studied. Given these premises, the study of alternative monomeric systems that could guarantee good reactivity and high functionalization possibilities appears intriguing. Within this field, 1,3-dioxolan-4-ones (DOXs) appeared as promising candidates. DOXs synthesis is straightforward and their high reactivity is ensured by the release of a small molecule (i.e. a ketone or aldehyde) during the polymerization, providing a strong driving force for the reaction. Albeit being promising monomeric systems for the synthesis of functionalized PLA-based materials, their chemistry has been scarcely investigated. For this reason, different DOX monomers bearing different substituents have been synthesized and both homo- and copolymerized, to yield PLA-based materials with variegated properties.

Organocatalyzed, solvent-free polymerization of lactic acid-derived DOX was optimized[1] and the conditions applied to an eugenol-functionalized monomer (EuDOX) to yield a biobased, recyclable thermoset.[2] Naturally occurring phenols as cardanol and carvacrol were employed as substituents for the synthesis of CardDOX and CarvDOX monomers respectively, which were successfully copolymerized with L-lactide yielding PLA based materials with tunable thermal properties.[3]

Styrene bearing DOX monomer (StyDOX) was successfully synthesized and exploited for the synthesis of polystyrene-polylactic acid copolymers, preventing phase separation phenomena and promoting self-assembly behavior. Finally, benzophenone-functionalized DOX (PhenDOX) was copolymerized with L-lactide, allowing to get light-sensitive PLA based copolymers.

These different examples were useful to scratch the surface of this innovative chemistry, showing its potential. Further studies will be carried out, aimed not only at the study of new substituents, but also at an optimization of the homo- and copolymerization conditions in order to expand even more the concept of functionalized PLA derivatives with tailored properties.

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Hybrid organic-inorganic materials based on polydopamine-like chemistry

Carla Calabrese,[a] Leonarda F. Liotta,[a] Carmela Aprile,[b] Loraine Soumoy,[b] Francesco Giacalone,[c] Michelangelo Gruttadauria [c]

[a] Istituto per lo Studio dei Materiali Nanostrutturati (ISMN-CNR), Via Ugo La Malfa 153, 90146, Palermo (Italy); [b] Dipartimento di Scienze e Tecnologie Biologiche Chimiche e Farmaceutiche, Università di Palermo, Viale delle Scienze Ed. 17, 90128, Palermo (Italy); [c] Département de Chimie, Université de Namur, Rue de Bruxelles, 5000, Namur (Belgium)

The design of multifunctional materials with hybrid features is a wide-ranging topic which covers many research fields such as gas storage, biosensors, drug delivery and catalysis. In the last few years, a paramount attention has been devoted to the so-called mussel-inspired materials based on polydopamine or polydopamine-like polymers [1] showing high potential for a broad spectrum of catalytic reactions [2]. In this context, the development of a sustainable catalytic process requires viable synthetic procedures combined with good activity, recoverability and reusability of the catalysts. In this scenario, a broad scope of hybrid organic-inorganic multifunctional materials has been prepared by mimicking the polydopamine chemistry. The synthetic procedure of polydopamine-like hybrids was based on the oxidation of catechol in conjunction with a plethora of organo-silane units bearing aliphatic amine and imidazolium moieties (Figure 1). The obtained materials were fully characterised by using several techniques such as nitrogen physisorption, thermogravimetric analysis, pH_{PZC}, ^{13}C and ^{29}Si solid state NMR, IR, X-ray photoelectron spectroscopies. Characterisation of these hybrids indicated the presence of several functional groups. The Knoevenagel reaction between ethyl cyanoacetate and several benzaldehydes was chosen as good probe to investigate the availability of functional groups on the surface. In such a way it was possible to identify the best reaction conditions and the use of the proper aminopropylsilanes for the obtainment of the most active catalytic materials. The most active hybrids were successfully tested in recycling procedures.

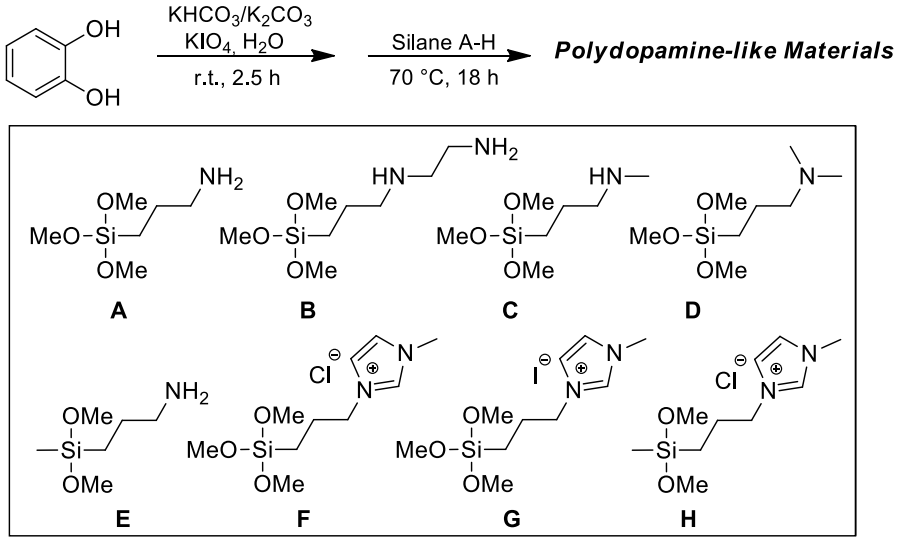

Figure 1. Polydopamine-like materials as heterogeneous catalysts for Knoevenagel reactions.

Acknowledgments: The work was carried out in the frame of the PRIN2017- 2017YJMPZN project.

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β-ketoimine Cr complexes for the production of functional polyolefins: exploring the metal-ligand bond as a key point of the catalysts

A. Piovano,[a] G. Zanchin,[b] A. Amodio,[a] F. De Stefano,[c] V. Guiotto,[a] B. Palucci,[b] R. Di Girolamo,[c] G. Leone,[b] E. Groppo[a]

[a] Department of Chemistry, INSTM and NIS Centre, University of Torino, Italy; [b] Institute of Chemical Science and Technologies, SCITEC-CNR, Milano, Italy; [c] Department of Chemical Sciences, Federico II University of Napoli, Italy.

In the last years, ecological concerns have pointed out the need of renewing the plastic economy, increasing its value-chain. To this purpose, we hereby present two Cr-based complexes (Figure 1a), to be used in combination with an Al-alkyl activator in the homogeneous catalysis for the production of functional polyolefins. The two complexes have been synthetized by reacting $CrCl_3$ with the same β-ketoimine ligand, either as such (1) or after deprotonation by *n*BuLi (2).

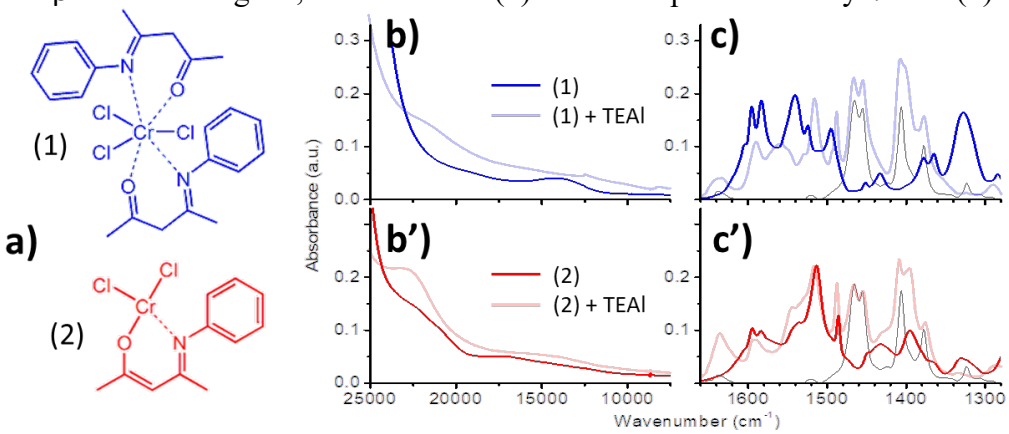

Figure 1. Part a) Structures of the two complexes on the base of elemental analysis. Parts b and c) UV-Vis and IR spectra of the two Cr complexes in chloroform before and after reaction with triethylaluminum (TEAl).

Both complexes proved to be active in the polymerization of ethylene and other cyclic olefins, which are the building blocks of functional polymers alternative to traditional commodities for a broad range of applications. Table 1 reports the results in norbornene (NB) polymerization; the produced polynorbornenes are semi-crystalline and highly stereoregular, with an unusual 2,3-*exo*-diheterotactic structure, previously reported only in a few cases in the literature.[1]

Table 1. NB polymerization in toluene ([NB] = 1 mol/L, [Cr] = 1 mmol/L, [Al]/[Cr] = 1000, T = 20 °C).

Catalyst	Yield (g)	Conversion (%)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
L_2CrCl_3 (1) + MAO	1.05	78	1790	1055	1.7
$LCrCl_2$ (2) + MAO	1.00	74	1740	1210	1.4

The overall catalytic behavior of the two complexes is actually comparable, although the β-ketoimine ligand plays an undeniable role since the same results cannot be obtained by $CrCl_3$ alone.

UV-Vis and IR spectroscopies (Figure 1b and c) have been applied to respectively investigate the electronic properties of Cr centers (which reflect their oxidation state and coordination) and the functional groups of the ligand (which are sensitive to the different interactions with the metal). The investigation of the complexes as such and after activation with different Al-alkyls has allowed unraveling at a molecular level the chemical interactions concurring to the catalytic process.[2]

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Self-Healing and Shape-Memory Hydrogels by Micellar Polymerization

Edoardo Podda, Diego Antonioli, Valentina Gianotti, Michele Laus

Department of Science and Technological Innovation, University of Eastern Piedmont, viale T. Michel 11, 15121, Alessandria Italy.

Hydrogels are three-dimensional polymeric network with the capability to absorb a large amount of water or biological fluids. Usually, these materials are made of hydrophilic crosslinked polymer chains able to swell in water and present a soft rubbery consistency similar to living tissues. For this reason, hydrogels are used for biomedical, biotechnology and pharmaceutical applications [1,2]. The crosslinker nature separates hydrogels in two large families namely chemical or physical crosslinked. In the former, crosslinking is obtained by covalent bonding the chains either during the polymerization or in a post polymerization process [3]. In the latter, hydrogels are obtained using physical interaction such as hydrophobic association, ionic bond or hydrogen bond.
In this work we prepared physically crosslinked hydrogels by radical micellar polymerization. This type of polymerization involves a hydrophilic monomer (acrylamide), a hydrophobic monomer (octadecylacrylate, C18A), a surfactant (sodium dodecyl sulfate), and a salt (sodium chloride). The polymerization was initiated using a redox initiator consisting of ammonium persulfate and sodium metabisulfite. In addition, a multifunctional monomer, divinylbenzene (DVB), was used with the aim of creating branched chains and evaluating their effect on the material characteristics. Three series of samples were prepared by varying the amount of octadecylacrylate and divinylbenzene.
The samples were characterized with thermal (DSC) and rheological analysis, both before and after each purification steps. As the concentration of C18A increases, the amount of water within the hydrogels decreases. In addition, the melting and crystallization enthalpies of the hydrophobic domains increase, and in a parallel fashion an increase in mechanical modulus G' takes place.
Furthermore, as the DVB concentration increases, the water content decreases, and the mechanical modulus G’ increases. This effect is probably due to the formation of additional chemical crosslinkings within the polymer network.
The self-healing behavior of these materials was also demonstrated by several rheology measurements and other specific experiment. As the DVB concentration increases, the self-healing efficiency decrease and so does the shape-memory behavior. Heating the materials above T_m, hydrogels could be deformed into different shapes that can be fixed on cooling. Then, heating again above T_m, the original shape is recovered. This effect can be observed only for samples containing more than 20% of hydrophobic monomer.

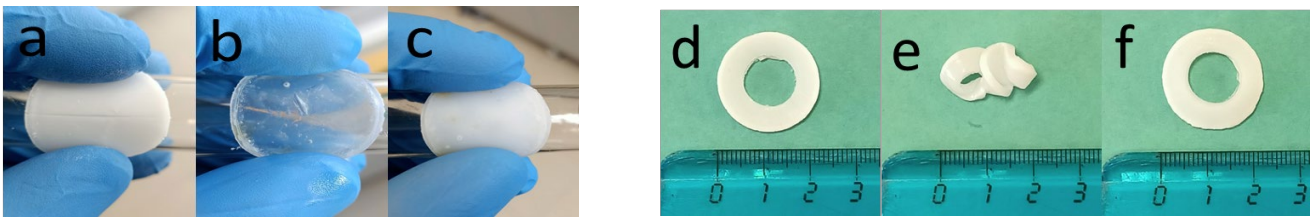

Figure 1. Sequence demonstrating self-healing (left) and shape memory (right) behavior. Incised material (a), self-healed material after 1h at 70°C (b) and then after 24h at room temperature (c). Original shape (d), temporary shape obtained by deforming material (e) and recovered shape after heating phase (f).

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Evidence of Preferential Grafting of Short Chains in Grafting To Reactions of Hydroxy-Terminated P(S-r-MMA) Copolymers

Riccardo Chiarcos[a], *Diego Antonioli*[a], *Valentina Gianotti*[a], *Michele Perego*[b], *Michele Laus*[a]

[a]*Department of Science and Technological Innovation, University of Piemonte Orientale, viale T. Michel 11, 15121, Alessandria Italy.*
[b]*Laboratorio MDM, IMM-CNR, Via C. Olivetti 2, 20864 Agrate Brianza, MB, Italy.*

Polymer brushes have captured the scientist interest for more than fifty years as surface modifiers and several theoretical and experimental papers were published on the topic. A privileged role in the polymer brush research is occupied by the development of technologies useful for the brush production. In this frame, *grafting to* reactions are most promising because they allow the anchoring of polymer chains that can be completely characterized before grafting. Classically, the grafting to process is conducted under the assumption that the average molecular weight of the tethered chains is exactly the same of the starting polymer. In this work we have demonstrated that this hypothesis is essentially wrong. In fact, several mixtures of poly (styrene-r-methyl methacrylate) and poly (deuterated styrene-r-methyl methacrylate) statistical copolymers with different molecular weights were grafted on silicon oxide substrates and analyzed by TGA-GC-MS, proving brush compositions significantly enriched by the shortest chains compared to the starting mixtures. The experimental data were then compared with the values predicted using a simple kinetics model based on polymer shape. A correlation between the brush enrichment of the shortest chains and the ratio of the molecular weights of the two polymers in the starting mixture was suggested according to the following equation.

$$r_{brush} = \left(\frac{N_L}{N_S}\right)^{\frac{1}{2}} r_{mixture} \qquad \text{Eq. 1}$$

In Equation 1, r_{brush} and $r_{mixture}$ represent the molar ratio between the short and the long chains in the brush and in the initial mixture, respectively. N_L and N_S are the degree of polymerization of the long and the short chains.
Because the physical properties of polymer brushes strongly depend on the molecular weight of the grafted chains, a correct design of a functionalized surface has to consider the polymer polydispersity and the preferential grafting of the short chains.

Axially oriented guest induced crystallization in syndiotactic polystyrene unstretched fibers

Antonietta Cozzolino, Paola Rizzo, Chiara Gallo, Christophe Daniel, Gaetano Guerra

Dipartimento di Chimica e Biologia "A. Zambelli", Università degli Studi di Salerno, Fisciano (SA), Italy

Crystalline phase orientations, axial and planar, can be generally obtained for polymers by axial and biaxial stretching, respectively[1,2]. For co-crystalline phases (CC) between polymer hosts and low-molecular-mass guest molecules, different kinds of planar orientations can be easily prepared, even in the absence of mechanical stretching. This phenomena have been deeply studied for syndiotactic polystyrene (s-PS)[3] and poly(2,6-dimethyl-1,4-phenylene)oxide (PPO)[4].

In particular for s-PS films, three different kinds of uniplanar orientations were obtained for δ clathratres (a//c//, $a_{\perp}$c//, a//$c_{\perp}$)[5] as well as for ε clathrates ($a_{\perp}$, $b_{\perp}$, $c_{\perp}$)[6] with orientation names based on the preferential parallel (//) or perpendicular ($\perp$) orientation of their crystal axes, with respect to the film plane. Uniplanar orientations of s-PS can be maintained not only after guest-exchange[7] but also after suitable guest removal procedures leading to nanoporous-crystalline (NC) δ[8] and ε[9] phases. High degrees of axial orientation can be obtained for s-PS by usual axial stretching procedures on polymer films and fibers as well as by high-speed melt spinning processes[10].

In this paper, we show that guest-induced crystallization of essentially unoriented amorphous melt-spun fibers can lead to high degrees of axial orientation of s-PS crystalline phases (in the range $0.7 < f_c < 0.8$). To our knowledge, this phenomenon is unprecedented for polymer fiber crystallization. High degrees of axial orientation can be also maintained in fibers exhibiting derived NC and dense s-PS crystalline phases.

The most relevant achievement of this paper is that by simple guest sorption procedures in amorphous s-PS fibers (as produced in pilot industrial plants) not only it is possible to obtain NC forms (suitable for removal of organic pollutants from the environment[11]) or CC forms with active guests (suitable, e.g., for antimicrobial release[12]) but also to get axial orientation that improves fiber properties[13], without mechanical stretching.

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Axially Oriented Co-crystalline Phases of Poly(2,6-dimethyl-1,4-phenylene)oxide and host-guest orientations

Manohar Golla, Baku Nagendra, Christophe Daniel, Gaetano Guerra, Paola Rizzo

Chemistry and Biology Department, University of Salerno, Fisciano (SA), Italy-84084

A commercial engineering thermoplastic polymer, poly(2,6-dimethyl-1,4-phenylene)oxide (PPO), forms co-crystalline (CC) phases with low molecular weight guest molecules, as well as nanoporous crystalline (NC) phases, after guest removal. This kind of behavior was observed in the past only for syndiotactic polystyrene (sPS). CC and NC phases of both polymers have received attention both in scientific studies as well as for possible applications. [1-5]
In this contribution we are describing the achievement of films exhibiting axially oriented nanoporous-crystalline (NC) and co-crystalline (CC) phases of PPO. Wide Angle X-ray diffraction (WAXD) patterns of these axially oriented films can contribute to establish the PPO crystal structures. Polarized FTIR spectra of these oriented films allow to establish relative orientations of host chains and guest molecules (Figure 1). [6,7]

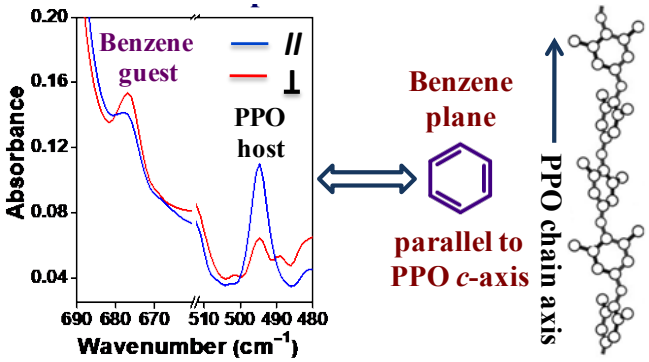

Figure 1. Polarized FTIR spectra of PPO/benzene co-crystalline *α* form

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Liquid crystal elastomer based artificial muscles for cardiac repair

Parmeggiani, Camilla[a,b,c], Martella, Daniele[b,c], Sacconi, Leonardo[b,d], Grandinetti, Bruno[b,e], Giulia Vitale[f], Tesi, Chiara[f], Wiersma, Diederik S.[b,c,e], Poggesi, Corrado[f] and Ferrantini, Cecilia[b,f]

[a]Department of Chemistry "Ugo Schiff", Università di Firenze, Sesto F.no, Italy; [b]European Laboratory for Non Linear Spectroscopy, Università di Firenze, Sesto F.no, Italy; [c]Istituto Nazionale di Ricerca Metrologica (INRiM), Torino, Italy; [d]National Institute of Optics, National Research Council, Sesto F.no, Italy; [e]Department of Physics and Astronomy, Università di Firenze, Sesto F.no, Italy; [f]Department of Molecular and Developmental Medicine, Università di Siena, Siena, Italy

Advanced materials, able to work as integrated actuators for the treatment of muscle injuries, could combine rapid and long-lasting intervention, which is the main goal in regenerative medicine. Among them, Liquid Crystalline Elastomers (LCEs) are biocompatible polymers able to reversibly deform in response to a given stimulus by generating movement. Once stimulated, LCEs can mimic muscle force production [1] resulting in a good advancement in regenerative medicine. However, their application in biology was limited by the slow response times and the reduced possibility to modulate tension levels during activation. Here we report how, by screening different monomeric formulations, biocompatible LCEs showing improved muscle-like characteristic were prepared. Combination of the improved Light responsive LCEs with different illumination solutions opened to the development of new solutions for the mechanical cardiac assistance.

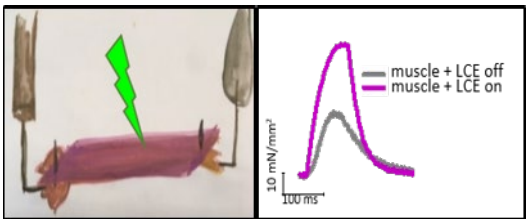

Figure 1 - Liquid crystalline elastomer (LCE) to assist cardiac contraction (below).

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Cell instructive polymers based on liquid crystals

Martella Daniele[a,b], Rojas Marta[b], Wiersma Diederik S.[a,b,c], Parmeggiani Camilla[b,d]

[a]Istituto Nazionale di Ricerca Metrologica (INRiM), Torino, Italy; [b]European Laboratory for Non Linear Spectroscopy, Università di Firenze, Sesto F.no, Italy; [c]Department of Physics and Astronomy, Università di Firenze, Sesto F.no, Italy; [d]Department of Chemistry "Ugo Schiff", Università di Firenze, Sesto F.no, Italy.

Control of the collective cells organization and their correct differentiation are key steps to reproduce biological tissues *in vitro*. So far, many attempts to prepare polymeric scaffolds that mimic the biological environment have been done, trying to reproduce the mechanical property or the extracellular matrix composition and topography. To date, cell differentiation protocols required scaffolds bearing micro/nanometric features or stimulated ones (by mechanical stretching or electric field). However, the complexity of these methodology strongly limits their wide application.

In this communication, we will show a totally different approach for the alignment and differentiation of several cell lines exploiting Liquid Crystalline (LC) polymers. Materials with anisotropic molecular structure and tunable rigidity have been prepared by photopolymerization of acrylate-based LCs and tested as support for cell growth (from human fibroblasts, C2C12 myoblasts and cardiomyocytes). We demonstrated LC polymers to present several advantages with respect to commercial scaffolds such as and improved adult-like dimensions and a more mature cell function of human induced pluripotent stem cell-derived cardiomyocytes (hiPSC-CMs) in a shorter time. [1] Furthermore, LC organization was demonstrated able to drive specific cells arrangements during myoblast cultures, as shown in Figure 1. Cell alignment was found to follow the nematic director thus demonstrating for the first time as the LC order inside the material can be translated to a living organism. [2] At the end, myotube maturation has been investigated with electrophysiological studies demonstrating as muscular fibres cultured on our LCs present better functional features with respect of those obtained on standard supports.

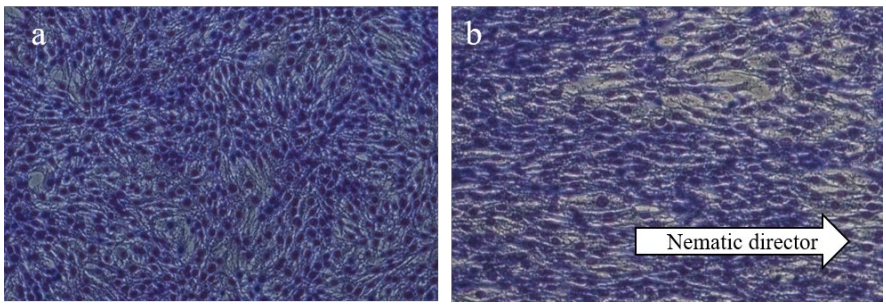

Figure 1: C2C12 culture on a Petri dish (a) and on a LC polymer (b).

Acknowledgments. The research leading to these results has received funding from MUR under the FISR program, project FISR2019_00320 Leonardo.

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Bio-based and waste-derived polyurethanes for energy systems

Mariotti Nicole[a], Bonomo Matteo[a], Galliano Simone[a], Viada Gabriele[a], Tunno Federica [b], Bonandini Luca[b], Menozzi Alberto[b], Quagliotto Pierluigi [a], Barolo Claudia[a,b,c]

[a] Dipartimento di Chimica, NIS Interdepartmental and INSTM Reference Centre, Università degli Studi di Torino, Via Pietro Giuria 7, 10125 Torino, Italy; [b]S.E. Special Engines S.r.l., Strada del Cascinotto 163, 10156 - Torino – Italy; [c]ICxT Interdepartmental Centre Università degli Studi di Torino, Lungo Dora Siena 100, 10153 Torino, Italy

Polyurethanes (PUs) are the most used polymers worldwide and they are involved in many applications such as rigid and flexible foams, coatings, elastomers, adhesives and sealants.[1] The traditional synthetic route for PU production involves polyols and diisocyanates and it is still widely dependant on fossil sources.[2] Moreover, the isocyanate synthesis is still performed via phosgene routes.[3]

In our work, we optimized the preparation of a new PU starting from bio-based and waste-derived materials through a Design of Experiment (DOE). In particular, the exploited reagents are (i) bio-based polyols mainly obtained from rapeseed and soy oils, (ii) the bis(2-Hydroxyethyl) terephthalate (BHET) obtained from the chemical recycling of PET[4] and (iii) bio-based diisocyanates.

The obtained polymer has been analysed through TGA, DSC, UV-VIS and IR techniques. Our purpose is to achieve high transmittance (good transparency) and thermal resistance to exploit this material as an encapsulant for perovskite solar cells and LED. The results are promising, also when compared with a commercial PU, and the polymer has up to the 40 % of bio-based and waste derived components meeting the requirements for more sustainable and circular polymers. A material decoupled from finite resources and intended to protect the energy systems is also strictly related to the Sustainable Development Goal 7 from UN for a “clean, reliable and affordable energy”.[5]

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Nanostructured Cu-based Electrocatalysts on a Carbonaceous Gas Diffusion Layer for the Electrochemical Reduction of CO_2

Martina Serafini [a], *Federica Mariani* [a], *Andrea Fasolini* [a], *Erika Scavetta* [a], *Domenica Tonelli* [a], *Francesco Basile* [a]

[a] *Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale del Risorgimento 4 40136, Bologna (IT)*

Among the most promising strategies to reduce the concentration of carbon dioxide in the environment, technologies using electrochemical approaches are one of the major challenges. In this scenario, the idea of the "artificial leaf" [1] capable of a "passive" CO_2 conversion to chemicals and fuels exploiting an electrical current where electrons are preferably gained from renewables, could become a sustainable and inexpensive solution of widespread use. For this purpose, copper-based electrocatalysts have been showing a very high selectivity towards hydrocarbons production [2] and, coupled with carbonaceous supports, they represent good candidates for the development of low-cost electrodes suitable for the aforementioned artificial photosynthesis.

In this contribution, we investigated the activity of several copper-based catalysts electrodeposited on a carbonaceous gas diffusion layer during the electrochemical liquid phase reduction of CO_2. Starting from a Cu^0 thin layer as active phase, obtained by a one-step electrochemical deposition on a 4 cm^2 sized carbon fiber paper (CP), we functionalized the surface using simple chemical and electrochemical methods. Cu_2O-Cu^0/CP was obtained by an electrochemical oxidation in 0.5 M KOH, $Cu(OH)_2$-Cu^0/CP was achieved by soaking the thin metal copper film in a mixture of $(NH_4)_2S_2O_8$ and NaOH, and CuO_x-Cu^0/CP by soaking the pristine Cu^0/CP in a mixture of H_2O_2 and NaOH. The performance of the four different catalysts for the electrochemical reduction of CO_2 in liquid phase was valuated, using a H-type cell equipped with and Ag/AgCl and a Pt gauze as reference and counter electrodes, respectively and employing 0.3 M $KHCO_3$ as electrolyte. It was demonstrated that Cu^+/Cu^0 was the most active redox Cu couple, showing the best selectivity and Faradaic Efficiency (FE). Indeed, at -0.4 V vs RHE, a FE of ~76% was obtained for acetate production, which was the main identified product.

In order to enhance the basicity of the catalyst and thus increase the CO_2 adsorption improving the catalyst activity, the electrosynthesis of a CuMgAl layered double hydroxide (LDH) catalyst over the same carbonaceous substrate was optimised, starting from a solution containing the nitrate salts of each cation. Afterwards, the LDH was chemically reduced with 0.1 M KNO_2 at 338 K so as to obtain a composite material of Cu^0-MgAl LDH. SEM-EDS analysis confirmed the presence of sub-micrometric metal copper particles within the LDH structure. The as-obtained electrocatalyst was then electrochemically oxidized in 0.5 M KOH. Finally, as preliminary tests, the pristine LDH and the activated composite were tested for the CO_2 electroreduction at -0.4 V vs RHE. In the optimised experimental conditions, the Cu-LDHs catalysts showed good selectivity towards acetate production.

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How to exploit thermochemical catalysts to make efficient & sustainable CO_2 electroreduction to added value products

Simelys Hernández, Hilmar Guzmán, Daniela Roldán, Federica Zammillo, Nunzio Russo

Catalytic Reaction Engineering for Sustainable Technologies (CREST), Department of Applied Science and Technology (DISAT), Politecnico di Torino, C.so Duca degli Abruzzi, 24, 1019, Turin, Italy.
e-mail: simelys.hernandez@polito.it, +39 011-0904774.

The electrocatalytic (EC) CO_2 reduction (CO_2R) driven by renewable energy can be exploited for the future energy transition, for the carbon storage into valuable products like syngas (H_2/CO mixtures), organic acids (formic acid) and chemicals/fuels (C_{1+} alcohols).[1,2] A big challenge for the industrialization of this technology is to find low-cost electrocatalyst, efficient reactors and process conditions. In our lab, we are exploiting the current knowledge of the thermocatalytic CO_2 hydrogenation to develop low-metal or noble-metal-free CO_2R electrocatalysts.[3] Our results open a promising path for the prospective implementation of metal-oxides nanostructures for the CO_2 conversion to the chemicals and fuels of the future. For instance, noble metals (e.g. Ag and Au) are highly used for syngas production.[4] To reduce the catalyst cost, we developed electrodes made of Ag nanoparticles (NPs) on TiO_2 nanotubes (NTs),[5] which were used as an efficient support, for enhancing the stability of key CO_2^- radical intermediate and decreasing the EC CO_2R overpotential. Moreover, Cu/Zn/Al-based catalysts producing methanol and CO from the CO_2 thermocatalytic (TC) hydrogenation (at H_2 pressure (P) of 30 bar and temperature (T) > 200 ºC) generates H_2, CO and other C_1 to C_3 liquid products like alcohols, during the electrochemical CO_2R in a gas-diffusion-electrode system at ambient T,P. We have also developed B,N-doped Cu oxide catalysts promoting the dimerization of the *CO intermediate and reaching 77% of selectivity towards formate and alcohols with a relevant current density. From an environmental and technoeconomic analysis applied to the case of study of the scaled-up methanol production, including downstream purification processes, we determined that optimized EC process conditions could lead to a practical implementation of this technology; that is, recirculation of the not reacted CO_2, achievement of current densities in the range of 100-200 mA/cm^2 with faradaic efficiencies (> 90%), and use of renewable electricity sources (*i.e.* 30% of the total energy).[3] Hence, considering the effective allocation of methanol on a real market scenario, the EC process results to be economically advantageous over the TC one at productivity scales as low as 19.1 kg/h, and could lead to a carbon footprint that is comparable to that of current industrial technologies for methanol production (climate change impact of 2.72 $kgCO_2/kgCH_3OH$). Moreover, in a scenario with a 100% renewable energy such as photovoltaic, it is possible to reach savings in that carbon footprint of up to 62%.

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High rate CO_2 electroreduction to formate with a InP colloidal quantum dots derived catalyst

Ivan Grigioni, [a, b] *Edward H. Sargent,* [b] *and Elena Selli* [a]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy*
[b] *Department of Electrical and Computer Engineering, University of Toronto, Ontario, Canada.*

CO_2 electrochemical reduction offers ways to recycle CO_2 at the emission point or from air, to produce fuels and chemical building blocks. When it is combined with electricity from renewable sources, CO_2RR may lead to the production of carbon emission-free chemical feedstocks [1].
Formate is among the commodity chemicals produced by CO_2RR and can be profitably converted to formic acid which is of interest as a hydrogen carrier for transportation. Electrocatalysts for selective formate production operating at high current densities will reduce the capital costs and 200 mA cm^{-2} at a full cell potential of 2.25 V is typically considered as a threshold for viability [2]. Larger current densities further decrease the capital contribution on product cost.
Inspired by the high selectivity to formate of indium-based catalysts and by the high activities achieved using nanostructured catalysts [3], we pursued InP colloidal quantum dots (CQDs) in the fabrication of cathodes sustaining formate production in the A cm^{-2} range. InP CQDs-based cathodes produced by depositing the InP CQDs ink on a carbon-based gas diffusion layer generate formate as the only liquid product with H_2 and CO as additional products. Selectivity, measured as Faradaic Efficiency (FE), maintained above 90% (**Figure 1**) in all the current density range [4], with a formate production rate as high as 17.4 mmol h^{-1} cm^{-2}. A set of *operando* electrochemical and *in situ* Raman characterizations, together with *ex situ* XPS analyses on fresh and spent cathodes, reveals that the active catalyst presents coexistence of surface sulfur, derived from the CQDs ligand, and metal In. Cooperative catalysis between In metal and surface sulfur sites allows for the high selectivity and activity of this InP CQDs derived catalyst. The ability of operating with high FE in a wide range of current density and at low applied voltage makes InP CQDs a versatile catalyst candidate for practical electrochemical CO_2 reduction.

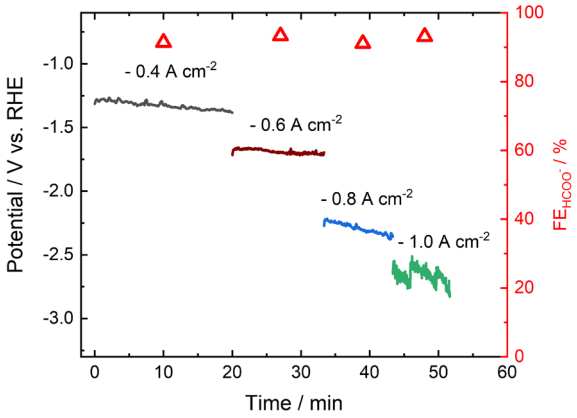

Figure 1. Stepped chronopotentiometry recorded from -0.4 to -1 A cm^{-2} in a flow cell with the cathode in contact with 3.0 M KOH; the right axis reports the Faradaic efficiencies.

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Preliminary investigation of anodic materials for potassium batteries

Daniele Versaci,[a] Lucia Fagiolari,[a] Federica Di Berardino,[a] Federico Giraldo,[a] Sabrina Trano,[a] Julia Amici,[a] Carlotta Francia,[a] Silvia Bodoardo,[a] Federico Bella[a]

[a] *Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 - Torino, Italy*

Future renewable energy integrated grid systems require rechargeable batteries with low cost, high safety and long cycle life. The much higher abundance of potassium compared to lithium in Earth crust indicates that rechargeable potassium batteries can represent an attractive replacement for lithium-ion counterparts. Rechargeable potassium batteries have gained tremendous attention during the past decade [1,2]. However, the development of rechargeable potassium batteries is still in its infancy.

Due to the large atomic radius of potassium, some electrode materials that are commonly used in Li-ion systems are not suitable for potassium batteries. Thus, anode materials for these energy storage systems are mainly based on carbon materials, metal alloys and potassium metal. On the other hand, cathode materials can be divided into three categories: Prussian blue and its analogues, layered metal oxides and polyanion oxides.

In this emerging field, the main challenges are: i) achieving a strong structural stability of newly developed electrodes; ii) inhibit the formation of potassium dendrites and build a stable electrode/electrolyte interface; iii) trying to find an electrode to be considered as a reference/standard system when evaluating the performance of newly synthesized compounds for anodes and cathodes. In this contribution, a systematic study of a series of potential systems for anodes in potassium batteries is presented, figuring out the most promising strategies to design lab-scale working devices.

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Solvothermal synthesis of doped hematite/reduced graphene oxide nanocomposites for sodium-ion batteries

Maria Grazia Musolino[a,e], Claudia Triolo[a,e], Beatrix Petrovičovà[a,e], Riccardo Ruffo[b,e], Salvatore Patanè[c,e], Lorenzo Spadaro[d], Saveria Santangelo[a,e]

[a] *Dipartimento di Ingegneria Civile, dell'Energia, dell'Ambiente e dei Materiali (DICEAM), Università Mediterranea di Reggio Calabria, 89122 Reggio Calabria, Italy;* [b] *Dipartimento di Scienza dei Materiali (DSM), Università di Milano Bicocca, 20125 Milano, Italy;* [c] *Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra (MIFT), Università di Messina, 98166 Messina, Italy;* [d] *Istituto di Tecnologie Avanzate per l'Energia (ITAE) del Consiglio Nazionale delle Ricerche (CNR), 98126 Messina, Italy;* [e] *Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), 50121 Firenze, Italy*

Large-scale energy storage systems (ESSs) have become a key technology in stable and sustainable energy supply for applications in stationary power units and smart electric grids. Rechargeable sodium-ion batteries (SIBs) are gathering attention as ESSs, thanks to the benefits of low cost and abundant sodium resource. However, the development of cost-effective, environment friendly, high-performance electrode materials, especially anodes, is still an open challenge for SIBs.

This contribution deals with the synthesis of nanostructured composites, consisting of doped hematite nanoparticles, anchored on reduced graphene oxide (α-Fe_2O_3:D@rGO), by one-step solvothermal approach. This technique allows anchoring Fe_2O_3 on the graphene sheets in one step and in absence of any chemical reducing agent. The effect of the nominal rGO content of the nanocomposites (30 or 50 wt%) and of the type of dopant (titanium or manganese) on their physicochemical properties and electrochemical performance as anode materials for SIBs is evaluated.

The composites are obtained by solvothermal reaction of ferrous acetate, a proper amount of titanium (IV) isopropoxide or manganese (II) acetate tetrahydrate and graphene oxide, carried out in a stainless steel autoclave at 170 °C.

Physico-chemical characterization data evidence the successful incorporation of dopant in the α-Fe_2O_3 lattice and the absence of its influence on the crystalline phase and morphology of the iron oxide nanoparticles. The results of the electrochemical tests show a better electrochemical performance in terms of specific capacity and capacity retention with respect to the anode based on the undoped α-Fe_2O_3@rGO.

Reductive Upgrading of Biomass Derived Furan promoted by Spent Lithium-Cobalt Batteries as an Efficient Heterogeneous Catalyst

E. Paone[a,b], M. Miceli[a], P. Frontera[a,b], F. Mauriello[a], G. Ye[c], E. Mousa[c], E. Bontempi [b,d]A. Malara[a,b]

[a] Dipartimento DICEAM, Università Mediterranea di Reggio Calabria, Loc. Feo di Vito, I-89122 Reggio Calabria, Italy; [b] Consorzio Interuniversitario per la Scienza e la Tecnologia dei Materiali (INSTM), Firenze, 50121, Italy; [c] Swerim AB, Box 812, 97125 Luleå, Sweden; [d] Università degli Studi di Brescia, Via Branze 38, 25123, Brescia, Italy

In the last years, a lot of research efforts from both academia and industry players in the recycling electronic waste. Lithium ion battery (LIB), containing cobalt oxides, represent a valid resource for the preparation of Co-based catalysts. By now, only few attempts are present in literature in the use of cobalt based catalysts directly obtained from spent LIB mainly devoted to the promotion of oxidative reactions [1,2]. Reductive catalytic processes gained a lot of attention since, once the lignocellulose is deconstructed, cellulose, hemicellulose and lignin fractions can be subsequently converted into platform chemicals, that can be further transformed into target molecules, added value chemicals, solvents and materials (Figure 1). Furfural (FUR) is surely one of two most used furan-based feedstocks since its chemical structure allows the preparation of various high-value-added chemicals [3].

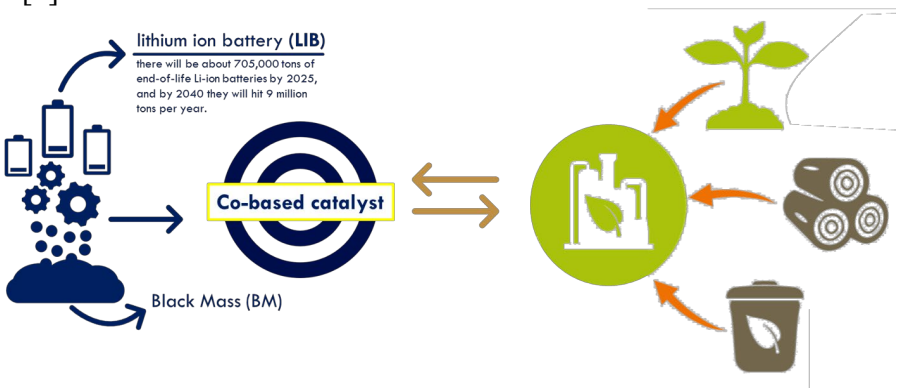

Figure 1. LIBs as readily available heterogeneous Co-based catalyst.

In this context, the present contribution, supported by NEXT-LIB EU project funded by ERA.MIN2, is focuses on a possible reuse of spent lithium-cobalt batteries as efficient heterogeneous catalysts (BM catalyst) for the reductive upgrading of different from lignocellulosic biomasses derived molecules. By using BM as the catalyst and 2-propanol as the H-source (CTH), under batch conditions, an appreciable FUR (0.1 M) conversion into Furfuryl alcohol (FAL) was achieved after 90 minutes at 120 °C. The conversion of BPE increased by increasing the reaction temperature and it was fully converted at 180 °C. In order to evaluate the stability of BM catalyst in the CTH of FUR, a series of consecutive recycling tests at 120°C for 90 min were performed. BM catalyst maintains its activity after five consecutive reactions and only slight changes in FAL yield were found, highlighting the good stability of the catalyst, that can be directly recycle (simple washing wit 2-propanol) for the next reaction run.

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Thermosetting polyurethanes resins: application as cheap, sustainable and scalable encapsulants for (flexible) Perovskite Solar Cells

Bonomo, Matteo [*a], *Taheri, Babak*[b], *Davide Gallo*[a], *Mariotti, Nicole*[a], *Bonandini, Luca*[c], *Matteocci, Fabio*[b], *De Rossi, Francesca*[b], *Zanetti, Marco*[a], *Brown, Thomas M.*[b], *Castro-Hermosa, Sergio*[b], *Segura Zarate, Ana Yancy*[a], *L. Angelo Castriotta*[b], *Menozzi, Alberto*[c], *Di Carlo, Aldo*[b], *Brunetti, Francesca*[b], *Barolo, Claudia*[a, d]

[a]*Dipartimento di Chimica, NIS Interdepartmental and INSTM Reference Centre, Università degli Studi di Torino, Via Pietro Giuria 7, 10125 Torino, Italy*
[b]*CHOSE - Centre for Hybrid and Organic Solar Energy, University of Rome ''Tor Vergata'' (IT)*
[c]*S.E. Special Engines S.r.l., Strada del Cascinotto 163, 10156 - Torino - Italy*
[d]*ICxT Interdepartmental Centre Università degli Studi di Torino, Lungo Dora Siena 100, 10153 Torino, Italy*

Perovskite Solar Cells (PSCs) are the most interesting emerging photovoltaic technology coupling very high efficiency with relatively low costs. Unfortunately, long-term stability of Perovskite Solar Cells PSCs is the main issue to be solved for a forthcoming commercialization. The stability of PSCs mainly suffers for water and oxygen infiltration as well as prolonged exposition to UV radiation. Hence, encapsulation of devices is mandatory to achieve good long-term stability [1,2]. Thermosetting Polyurethane resins (PU) are cheap and environmental-friendly materials whose mechanical, chemical and physical properties could be easily tuned by thoughtful choice of their precursor.

In this work we proposed to use this class of materials as encapsulant for (flexible) perovskite solar cells [3]. We focused our attention on the barrier properties of PU, especially in the prevention of degradation caused by both moisture and oxygen.[4] To test their UV and thermal stability, PU were stressed by means of various approaches: soaked with UV radiation and thermally stressed (i.e. 100 °C / -50 °C). Remarkably, both UV-vis and IR analyses of polymers did not show any significant modification of both mechanical and optical properties as a consequence of the activity.

When the PU were deposited on perovskite solar cells, the photoelectrochemical properties of encapsulated device remain constant up to three months. Notably, the incapsulated cells showed excellent stability stored under ambient light with RH > 50% and temperature < 30 °C by retaining 94% of the initial power conversion efficiency after more than 2500 hours whereas unprotected device lost more than 90% of their performance during the same period.

These results are quite remarkable as they demonstrate for the first time the use of modified polyurethanes as promising encapsulant materials for PSCs. Additionally, PU were also employed as encapsulant for modules.

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Low Temperature Methane Steam Reforming in a H_2-selective Pd Membrane Reactor

Andrea Fasolini[a], Salvatore Abate[b], Gabriele Centi[b] and Francesco Basile[a]

[a] *Dipartimento di Chimica Industriale "Toso Montanari", Alma Mater Studiorum-Università di Bologna,*
[b] *Dipartimento di Scienze chimiche, biologiche, farmaceutiche e ambientali, Università di Messina.*

Pure hydrogen production from methane is a multi-step process, which is run on a large scale for economic reasons, and is characterized by a steam reforming reactor, two water gash shift ones and two separation units of CO preferential oxidation and pressure swing adsorption. However, hydrogen can be produced in a one-step continuous process suitable for small scale applications, namely the Low Temperature Steam Reforming (LTSR) of methane in a membrane reactor. Here, the Steam Reforming is carried out in a reactor whose walls are composed by a membrane which is selectively permeable to hydrogen. Pd is the most used material for such application due to its high permeability and selectivity toward hydrogen [1]. However, the Pd layer deteriorates at temperatures higher than 500°C and for this reason the operative temperature of the Steam Reforming reaction, which usually runs around 900°C, must be lowered. This has a bad influence on the equilibrium yields that decrease due to thermodynamics and for this reason producing hydrogen by LTSR seems to be counterintuitive. However, the employment of a membrane reactor allows to produce high yields even at these temperatures thanks to hydrogen removal, which shifts the reaction toward the products, and concurrently, purifies hydrogen, as demonstrated in this work.
LTSR test were first tested in a classical fixed bed reactor with the aim of selecting the most suitable catalyst for the membrane reactor tests, which should be active, to provide high hydrogen partial pressure to favour separation and stable, to avoid time-consuming shut-downs and start-ups. Following previous results, a microemulsion synthesis [2,3] was selected to produce a $Ce_{0.5}Zr_{0.5}O_2$ and a ZrO_2 catalyst which were impregnated with Rh and reduced at different temperatures. Rh-ZrO_2 proved to be the most suitable catalyst and was charged in the membrane reactor. The effect of temperature, total pressure and sweep gas ratio were investigated. Methane conversion increased with temperature (Figure 1A). and pressure. The latter also favoured pure hydrogen recovery, as permeation is driven by the difference in hydrogen partial pressure between the two sides of the membrane. This was also increased by raising the sweep gas ratio, which decreased hydrogen partial pressure at the permeate side. Interestingly this also increased methane conversion and hydrogen production. In fact, methane conversion in the LTSR membrane reactor was much higher than the equilibrium conversion predicted for an analogous fixed bed reactor. Conversion as high as 65% (against eq. conversion of 15% for fixed bed) were obtained with hydrogen recoveries over 90% which were among the highest recoveries reported under the investigated conditions.

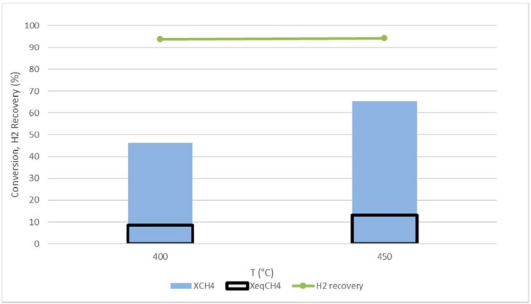

Figure 1: Experimental and equilibrium conversion as function of temperature and comparison of conversion and hydrogen recovery reported in literature for Pd-based membranes.

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Visible-light-driven coproduction of diesel precursors and hydrogen from lignocellulose-derived methylfurans

Tiziano Montini,[a] Nengchao Luo,[c] Emiliano Fonda,[c] Feng Wang,[b] Paolo Fornasiero[a]

[a] Department of Chemical and Pharmaceutical Sciences, INSTM Trieste Research Unit and ICOOM-CNR Trieste Research Unit, University of Trieste, Italy; [b] State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China; [c] Synchrotron SOLEIL, Saint Aubin, Paris, France.

Photocatalytic hydrogen production from biomass is a promising alternative to water splitting thanks to the oxidation half-reaction being more facile and its ability to simultaneously produce solar fuels and value-added chemicals. We demonstrated the coproduction of H_2 and diesel fuel precursors from lignocellulose-derived methylfurans via acceptorless dehydrogenative C−C coupling promoted by Ru-doped $ZnIn_2S_4$ photocatalyst under visible light irradiation [1]. With this process, up to 1.04 g $g_{catalyst}^{-1}$ h^{-1} of diesel fuel precursors (~ 41% of which are precursors of branched-chain alkanes) are produced with selectivity higher than 96%, together with 6.0 mmol $g_{catalyst}^{-1}$ h^{-1} of H_2, with a remarkable apparent quantum yield reaching a maximum of 15.2%. Subsequent hydrodeoxygenation reactions yield the desired diesel fuels comprising straight- and branched-chain alkanes. Detailed characterization of the Ru-doped photocatalyst by the extensive use of complementary techniques allowed to highlight that the reaction proceeds through a radicalic mechanism and to investigate the role of Ru as dopant. We suggest that Ru dopant ionss, substituted in the position of indium ions in the $ZnIn_2S_4$ matrix, improve charge separation efficiency, thereby accelerating C−H activation for the coproduction of H_2 and diesel fuel precursors. Recently, the study was extended to $ZnIn_2S_4$ photocatalyst modified with metal co-catalysts produced by photodeposition. Among all the tested metals, Pt co-catalyst showed the imporoved performance in the production of diesel-fuel precursors from 2,5-dimethylfuran. Moreover, a promoting effect of H_2O addition (below 10 wt%) in the reaction mixture was observed for $Pt/ZnIn_2S_4$. The detailed characterization of the used photocatalysts evidenced that Pt is atomically dispersed on the surface of the material and that H_2O in involved in the reaction mechanism, favoring the production of the radicals by activation of the C−H bonds of the methyl groups. The results presented in this work open the possibility to produce large amounts of liquid diesel fuel from a renewable second generation raw materials, like lignocellusosic residues, with the extensive exploitation of solar light.

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Improved water stability of $CsPbBr_3$ thin film photoelectrodes

Nicola Sangiorgi, Linda Bergamini, Alessandra Sanson

CNR-ISTEC, Via Granarolo, 64, 48018 Faenza (RA), Italy

In the last decades, all-inorganic thin film perovskite ($CsPbX_3$ with $X=I^-$, Br^-, Cl^-) has been received a lot of attention in the field of photovoltaics and optoelectronics due to their large absorption coefficient and excellent photoelectric properties with long carriers diffusion length. Recently, $CsPbBr_3$ materials has been successfully applied for water splitting and carbon dioxide reduction via photo-electrochemical cells (PECs) [1,2]. However, in order to develop a more environmental-friendly and sustainable technology, the water instability of $CsBrBr_3$ must be overcome. In this work, $CsBrBr_3$ nanocrystals were prepared by oleate synthesis and subsequently deposited by spin coating on transparent conducting substrate. Two different protective and catalytic coatings based on platinum and carbon were used to improve the $CsPbBr_3$ stability in water. These composite photo-electrodes were fully characterized from optical, morphological, and electrochemical points of view. The obtained results show an improved aqueous stability of the $CsBrB_3$ thin film with a substantial retention of the optical and electronic properties. Impedance analyses and photo-electrochemical characterization were used to determine the chemical properties of the new interface created between $CsPbBr_3$ and the two different coatings. The as-obtained $CsPbBr_3$-coating electrodes showed electronic properties suitable for solar-driven photo-catalytic reactions (water splitting or carbon dioxide reduction) in water. With this approach, the chemical and water stability of $CsPbBr_3$ thin films were enhanced making these materials adequate for sustainable photoelectrochemical cells technologies.

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Luminescent Solar concentrators based on Aggregation-Induced Emission

[a] Cosimo Micheletti; [a] Antonino Oliveri; [a] Francesco Ventura; [a,b] Tarita Biver; [a] Andrea Pucci

[a] Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy;
[b] Department of Pharmacy, University of Pisa, Via Bonanno Pisano 6, 56126 Pisa, Italy

A promising path to cost-effective photovoltaic (PV) systems is sunlight concentration. Over classical non-imaging geometrical concentrators, luminescent solar concentrators (LSCs) possess several advantages: low cost and weight, elevated theoretical concentration factors and aptitude to efficiently working with diffuse light without tracking or cooling equipment. However, although considerable progress made, current LSC-PV systems attain low power conversion efficiencies due to critical processes that hinder their ability to deliver light to PV cells, including fluorescence quenching due to dye aggregation. Different strategies have been adopted in the literature to overcome this issue, such as more compatible polymers or highly efficient emissive dopants [1]. In this case, fluorophores with aggregation-induced emission (AIEgens) have been proposed thanks to their high Stokes shift and quantum yield in the solid-state [2]. AIEgens are non-emissive when dissolved in good solvents but became highly luminescent in poor solvents or solid-state, thus circumventing the issues associated with fluorescence quenching due to dye aggregation also when dispersed in polymers. This study reports the use of two red-emitting AIEgens based on perylene bisimide and tetraphenylethylene cores as advanced fluorophores for thin-film (25±5 μm) LSCs (Figure 1). As polymer matrices, poly(methyl methacrylate) (PMMA) is selected as the standard, but experiments are also performed with alternative poly(cyclohexyl methacrylate) (PCMA) [3] and poly(vinyl butyral) (PVB) polymers. Investigations of the LSCs optical characteristics and performances yield maximum optical efficiencies of 11%, i.e. close to that of the current state-of-art of similar devices based on perylene-based fluorophores as Lumogen Red.

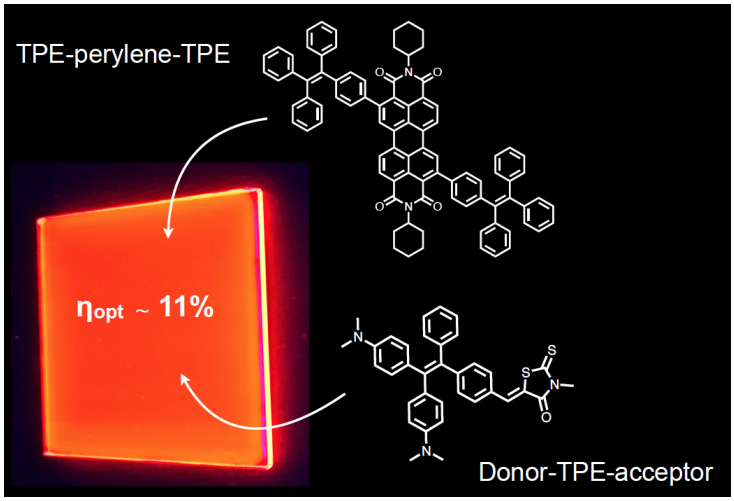

Figure 1. Thin-film LSC and chemical structures of the investigated

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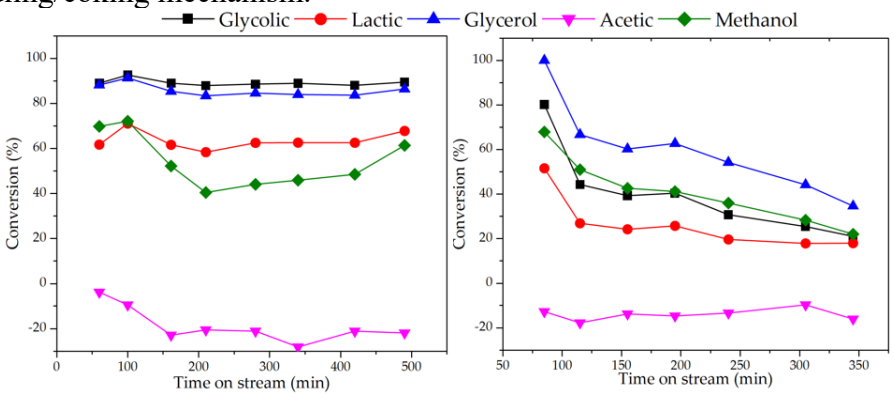
Green hydrogen production from wastewater derived from lignin-rich hydrothermal liquefaction

Giulia Zoppi [a], Giuseppe Pipitone [a], Samir Bensaid [a], Andrea Maria Rizzo [b], David Chiaramonti [b, c], Raffaele Pirone [a]

[a] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Turin, Italy. [b] Renewable Energy Consortium for Research and Development (RE-CORD), Viale Kennedy 182, 50038, Scarperia e San Piero, Italy. [c] "Galileo Ferraris" Energy Department, Politecnico Di Torino, Corso Duca Degli Abruzzi 24, 10129, Turin, Italy

Hydrothermal processes of biomass can lead to renewable fuels. For example, the hydrothermal liquefaction (HTL) of lignocellulosic biomass produces a biocrude with higher heating value and stability then the one obtained by pyrolysis, thanks to the lower oxygen content. However, the management of the aqueous by-product is an important bottleneck in the development of such technologies. It has been estimated that the cost of aqueous by-products disposal is second only to feedstock's cost. For this reason, the water fraction should be valorized. In this work, the aqueous phase reforming (APR) has been investigated with a double goal. First, it can convert the carbon-laden aqueous phase into a hydrogen-rich gas mixture, providing the hydrogen necessary for the upgrade of the bio-crude [1]; second, it can clean the aqueous phase that can be recycled to the liquefaction step, reducing the need for water make-up. Aqueous phase reforming has been tipically studied with model compounds, like poly-alcohols [2]. In the present work, a real aqueous-phase derived from lignin-rich HTL was used as a feedstock. The tests were performed in a continuous fixed-bed reactor, using a developmental 5% Pt/C catalyst by a commercial supplier. The influence of several reaction conditions was investigated, such as temperature, weight-hourly space velocity, co-feeding of an inert weeping gas. Beside the use of a real aqueous phase, a synthetic representative mixture was employed to highlight differences in the reactive behavior. Among the obtained results, in Figure 1, a comparison between the synthetic and real mixtures is reported. It is highlighted that the synthetic mixture showed a stable conversion of the reactants (glycolic and lactic acid, glycerol, methanol), while acetic acid was indeed produced by side-reactions. On the other hand, the real mixture reported deactivation phenomena after 250 min. The study of the textural properties of the catalyst reported that the surface area decreased, suggesting a deactivation by fouling/coking mechanism.



Sample	BET surface area (m^2/g)
Fresh	965
Synthetic	968
Real	618

Figure 1. APR of synthetic (left) and real (right) mixtures. Reaction conditions: 0.8 mL/min feed flowrate, 1 g Pt/C, 270 °C.

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H_2 production by photoreforming of glucose

F. Conte[a], G. Casalini[a], A. Tripodi[a], G. Ramis[b] and I. Rossetti[a]

[a] Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano, CNR-ISTM and INSTM Unit Milano-Università, via C. Golgi 19, 20133 Milan; [b] Dip. Ing. Chimica, Civile ed Ambientale, Università degli Studi di Genova and INSTM Unit Genova, via all'Opera Pia 15A, 16145 Genoa

A possible technology to valorise the sugars-rich processed liquor of pulp industry is the photoreforming of carbohydrates, i.e. water splitting for H_2 production assisted by organic molecules acting as hole scavengers (HS) in substitution of the slow oxygen oxidation reaction. In this way electron-hole separation is prompted under illumination, improving H_2 evolution productivity.
The aim of this work was to perform catalysts screening to assess the best performance among different surface decorated samples of nanosized titania. The effect of thermal treatments to induce structural modifications and defects formation was also explored.
The catalysts were prepared using either commercial P25 titania by Evonik or a home-made nanostructured titania prepared by flame spray pyrolysis. Metal decorated samples were prepared by adding 0.1-1% noble metals (Pt, Pd, Au, Ag) by impregnation or sol immobilisation.
Samples containing 0.1% Pt were subject to specific reduction/calcination treatments for 2-8 h at temperature 400-700°C either in H_2 or N_2 to check the effect of morphologic, structural and textural modifications or the possible partial reduction of Ti^{4+} to Ti^{3+} with formation of oxygen vacancies.
Activity tests were carried out in an AISI 316 head-flanged micro-pilot batch photo-reactor with cylindrical shape. UV radiation was provided by a 125 W double bulbed medium pressure Hg vapour lamp, located vertically in the axis of the reactor. The desired temperatures were reached by flowing heating/cooling water into the reactor jacket from an heating/cooling bath. Operating conditions were: Temperature 80°C, Pressure 4 bar of N_2, HS concentration 5-15 g/L, Photocatalyst concentration 0,25 g/L, Testing time 5h. pH was always kept neutral or naturally established.
The highest H_2 productivity and glucose conversion achieved among all the catalysts was obtained with a 0.1% mol Pt/P25 catalyst that underwent a post-activation thermal annealing at 400 °C in N_2 for 4h. H_2 productivity was 4.3 mol kg_{cat}^{-1} h_{irr}^{-1}, in accordance with literature reported results published until now regarding glucose photoreforming (maximum value reported for metal loaded catalysts was ca. 5.7 mol kg_{cat}^{-1} h_{irr}^{-1}), while glucose conversion was 13 % after 5 h irradiation.
Simulated processed black Kraft liquors were taken as an example of spent biomass derived waste water that can be a possible substrate for photoreforming, to produce a valuable energy vector while depurating water. The liquors were photoreformed using 1,0% wt Au_6Pt_4/P25 and 0,1% mol Pt/P25, two of the best performing catalysts with model carbohydrates. In both cases H_2 productivity was lower than with pure glucose, while CO_2 and ethane were the main products (2.7 and 3.4 mol kg_{cat}^{-1} h_{irr}^{-1} respectively for 1.0 wt% Au_6Pt_4/P25, and 3.1 and 4.6 mol kg_{cat}^{-1} h_{irr}^{-1} for 0.1% mol Pt/P25). This may be due to the combined effect of photo-Kolbe decarboxylation, α-carbon radical dimerization, dicarboxylic acid intermediates dehydration and hydrogenation and finally pH_{PZC} H^+ shielding effect. Carbon conversions to gaseous products were both higher than 15%, suggesting easier degradation pathways for hydroxy-dicarboxylic acid derived from sugar degradation.
Simulated processed sulfite spent liquors were photoreformed on 0.1% wt Pt/P25. H_2 and by-products productivities were instead very low. This can be ascribed to sugar surface crowding effect due to too high HS concentration, which could cause active site blocking. Moreover, since liquor pH is acid and lower than pH_{PZC} of TiO_2, an H^+ repulsive shielding effect prevents H_2 evolution.
Catalysts characterisation confirmed that the coexistence of a double anatase/rutile phase was determinant to achieve sufficiently high activity, together with a significant role of titania reduction, with formation of oxygen vacancies.

New biodegradable catalysts for photo-Fenton like process for wastewater treatment reuse in a circular economy perspective

Prisco Prete [a], Antonino Fiorentino [a], Luigi Rizzo [b], Raffaele Cucciniello [a], Antonio Proto [a]*

[a] *Environmental Chemistry Group (ECG), Dep. Chemistry and Biology, University of Salerno, Via Giovanni Paolo II, 132 Fisciano (SA), Italy*

[b] *Dep. Civil Engineering, University of Salerno, Via Giovanni Paolo II, 132 – 84084 Fisciano (SA), Italy*

**pprete@unisa.it*

Among all the most effective advanced oxidation processes (AOPs) for urban wastewater treatment Fenton and photo-Fenton process in the presence of $FeSO_4/H_2O_2$ is one of the most investigated. These processes have not been implemented at full-scale due to the requirement of strongly acidic pH (generally pH < 3) in order to prevent iron precipitation as hydroxide [1-2]. To overcome this limitation, some alternative processes have been proposed in the last years, including electro-Fenton, heterogeneous-Fenton and Fenton like, which involves either iron chelates or other transition metal - based complexes as soluble catalysts for the activation of H_2O_2 [3-5]

Thus, the development of new suitable ligands from renewable resources able to promote the Fenton like and photo-Fenton like processes for wastewater treatment have been presented in literature to meet the Green Chemistry principles for the preparation of new bio-degradable environmental catalysts through a benign-by-design approach. [6]

In this work, we report on the preparation, characterization and application of iminodisuccinate (IDS) metal complexes (M-IDS).

M-IDS catalysts have been tested as suitable catalysts in Fenton like and photo-Fenton like processes at neutral pH for the degradation of a model compound (phenol, 50 mg/L initial concentration) in water.

Encouraging results have been obtained with photo-Fenton like processes, achieving complete mineralization of phenol (95%) after 60 minutes of treatment.

The applicability of these metal complexes has been also extended to industrial wastewater treatment (olive oil mill wastewater) with excellent results in terms of COD removal.

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One-pot synthesis of TiO_2-rGO photocatalysts for the degradation of groundwater pollutants

S. A. Balsamo[a], R. Fiorenza[a], M. Condorelli[a], V. Scardaci[a] and S. Scirè[a]

[a] *Università degli Studi di Catania, Department of Chemical Sciences.*

Titanium dioxide (TiO_2) is the most employed semiconductor in photocatalysis thanks to its properties. However, two attributes damp its use: the first is the light absorption only in the UV region, which limits the utilization under solar light, and the second is the fast charge recombination that decreases its surface photocatalytic activity[1]. Several approaches to overcome these limitations have been investigated, including surface modification, doping, use of semiconductor or metal based co-catalysts[2] and carbonaceous materials sensitization. In particular, reduced graphene oxide (rGO) has emerged as one of the most promising materials thanks to its good conductivity coupled with an excellent interaction with TiO_2 surface favoured by the oxygenated groups on the rGO surface[3]. In this work, we present a comparison among three different approaches to prepare TiO_2-rGO nanocomposite photocatalysts, based on photoreduction or thermal treatment, in order to avoid the conventional hydro-solvothermal synthesis, that requires high pressures, and to save several steps in a large-scale application. The photocatalysts were tested in the solar photodegradation of a widely used herbicide (2,4-Dichlorophenoxyacetic acid, 2,4-D), to establish the most performing preparation approach. Briefly, the samples were prepared starting from TiO_2 P25 and GO in ethanolic suspension with a 2 wt % content of GO. Then, they were irradiated with UV and solar radiation to obtain respectively TiO_2-rGO UV and TiO_2-rGO solar samples. Instead, the thermal treatment was carried out in dry condition at 230 °C, to obtain the TiO_2-rGO thermal sample. The materials were characterized via N_2 adsorption-desorption measurements, DRS, Raman and FT-IR spectroscopies. Further, the degradation products were investigated via mass spectrometry and the toxicity of materials was tested on bacterial cells. Figure 1 shows the photodegradation results. The photolysis curve suggests the high stability of 2,4-D under irradiation. The best results (65 % degradation after 4h irradiation) were obtained with photo-reduced samples, exhibiting the same behaviour throughout all the measure. This could be related to a better reduction of the graphene oxide compared to the thermal treatment, as confirmed by Raman analysis. The untreated sample (TiO_2-GO) shows the same activity than the bare TiO_2, probably due to the low conductivity of the graphene oxide. On the other hand, although the graphene oxide reduction was confirmed by Raman, the thermal treatment led to a worsening of the photocatalytic activity that can be related to the lower BET surface area induced by heating. These results point to an interesting and convenient employment of solar treated sample in a one-pot preparation and utilization.

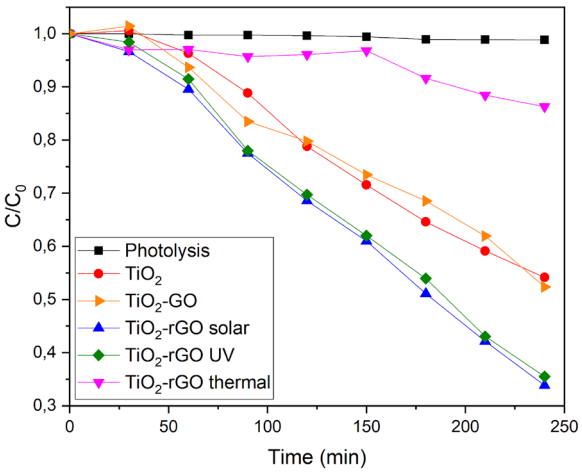

Figure SEQ Figure * ARABIC 1 2,4-D

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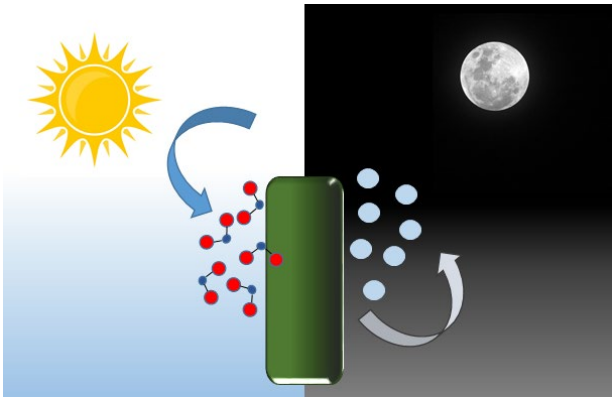
Efficient day-and-night NO_2 abatement by polyaniline/TiO_2 composites

Claudia L. Bianchi,[a,b] Daniela Meroni,[a,b] Carolina Cionti,[a] Marcela Frias Ordoñez,[a] Marta Sartirana,[a] Ermelinda Falletta[a,b]

[a] *Department of Chemistry, University of Milan, via C. Golgi 19, 20133, Milan, Italy*
[b] *Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), via Giusti 9, 50121 Florence, Italy*

The abatement of NOx emission represents a global concern in the field of environmental pollution. In this respect, costly approaches, using high reaction temperatures are required. However, innovative strategies have been proposed based on photocatalytic NOx abatement [1, 2].
Thanks to its chemical stability, wide availability, low cost, and reliable structure/electronic properties TiO_2 is one of the most investigated photocatalyst for NO_x photocatalytic oxidation [3, 4]. However, even though TiO_2 is highly active under UV light irradiation, its activity under sunlight is very low [2]. To address this disadvantage, the surface of this material can be properly modified by doping strategies or by coupling with other semiconductors, such as titanate perovskite [2]. Nevertheless, although these materials offer interesting alternatives under light irradiation, by the night photocatalysis is completely inactive.
In order to overcome this limitation, new day and night active materials have to be developed. In this regard, polyaniline (PANI), one of the main exponent of the class of conducting polymers, could represent an important alternative, allowing to exploit its redox properties, related on the presence of imino-quinoid/amino-benzenoid groups.
In the present study, PANI/TiO_2 composites were fabricated by an innovative green UV-assisted procedure, characterized by a combination of structural, morphological, and spectroscopic techniques, and applied to the NO_x abatement under both UV/LED light irradiation and in dark conditions. The amount of PANI in the final composite was accurately dosed in order to enhance the night-time activity without affecting photocatalytic properties. The role of PANI in the NO_2 abatement was also investigated on the basis of their physicochemical characteristics. The best materials were subjected to recycle tests in order to demonstrate their stability under the reaction conditions.



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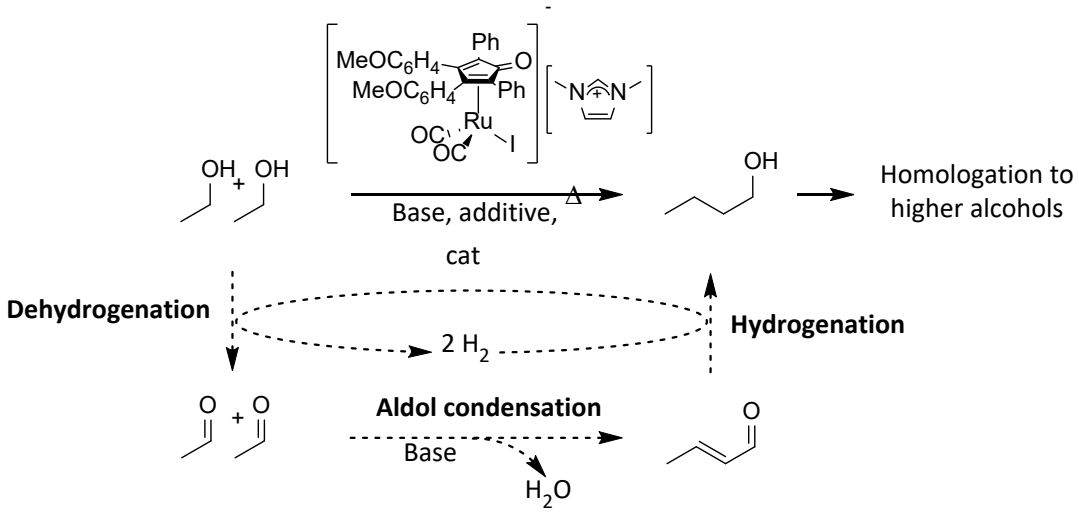
Upgrading of Ethanol: Boosting the Guerbet Reaction with a Redox Co-Catalyst

Anna Gagliardi,[a] Cristiana Cesari,[a] Alessandro Messori,[a] Nicola Monti,[a] Carlo Lucarelli,[c] Tommaso Tabanelli,[a] Valerio Zanotti,[a] Stefano Zacchini,[a] Fabrizio Cavani[a] and Rita Mazzoni[a]

[a]Dipartimento di Chimica Industriale "Toso Montanari", viale Risorgimento, 4 40136 Bologna.[c]Dipartimento di Scienza e Alta Tecnologia – Università dell'Insubria-Como, via Valleggio, 9, 22100 Como.

The Guerbet reaction is the catalytic upgrading of alcohols to a mixture of heavier and often branched analogues mainly used for advanced biofuel and lubricants applications. Second-generation biomass-derived ethanol can serve as a feedstock for this transformation, which has been receiving increasing attention and represents a promising route to obtain valuable products from renewable biomass.[1] The overall reaction can be split up into three steps: dehydrogenation, aldol condensation, hydrogenation (Scheme 1).



Scheme 1. Guerbet reaction process

Our group recently reported on an innovative and efficient homogeneous catalyst, characterized by the presence of an ionic ruthenium complex, which is able to activate the Guerbet process in mild conditions in the presence of a basic co-catalyst (e.g. sodium ethoxide, NaOEt).[2]
Here we report on a significant improvement of the catalytic system due to the addition of an electron transfer mediator,[3] which is likely acting as a catalytic "hydrogen storage" contributor. Thus, a parallel side reaction involving the catalyst in hydrogen evolution is avoided, leading to unprecedented conversions and almost complete overall selectivity. The catalytic system can be recycled and the reaction, at first studied on commercial absolute ethanol, shows comparable efficiency on a real matrix (head and tail waste from alcohol distillation) even in the presence of a significant amount of water.

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Sustainable process design for the valorization of bioethanol as platform chemical

I. Rossetti[a], A. Tripodi[a], F. Conte[a] and G. Ramis[b]

[a] Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano, CNR-ISTM and INSTM Unit Milano-Università, via C. Golgi 19, 20133 Milan; [b] Dip. Ing. Chimica, Civile ed Ambientale, Università degli Studi di Genova and INSTM Unit Genova, via all'Opera Pia 15A, 16145 Genoa

Process design is facing fully new challenges to adapt logical and economic successful schemes to new biorefinery concepts. The search for environmentally sustainable chemical processes needs to cope with limited scale up possibilities, complex reactants or products and new paradigms for the economic assessment of chemical plants. In this frame, we have selected bioethanol as platform chemical and pivot for the production of many intermediates and commodities, focusing on the target production scale of a sugar biorefinery. The examples considered were the production of syngas, hydrogen, bioethylene, bioethylene oxide and bioacetonitrile. After designing a fully integrated plant for each application we proceeded to the economic assessment, finding the key limits for the industrial implementation of the process.

In most cases, e.g. for the production of hydrogen and syngas, the cornerstone for the economic feasibility was the availability of a cheaper raw material, i.e. diluted bioethanol (40-50 wt%). The calculated minimum hydrogen selling price was 1.91 USD/kg, to be compared with a present standard value from methane steam reforming of 1.80 USD/kg. This calculation was made for a system capable of producing 7793 ton/year of H_2 starting from 40000 ton/year of bioethanol.

Also for bioethylene production we have experimentally demonstrated the possibility to use diluted bioethanol even for this dehydration reaction, operating at slightly higher temperature than with anhydrous ethanol. Accordingly, a full process flowsheet was designed, whose economic assessment demonstrated the possibility to produce bioethylene with 1.15-3.03 USD/kg production cost depending on the cost of diluted bioethanol (0.30-1.00 USD/kg), in many scenarios competitive with the current production cost in different countries.

Finally, another C2 compound with huge industrial applications is ethylene oxide, which may be in principle obtained in two steps following the route bioethanol → bio-ethylene → bio-ethylene oxide. This is the basis of the CRODA process currently proposed for the production of bio-derived ethylene oxide. Recently, a one-pot synthesis has been proposed, considerably simplifying the production process. Accordingly, we designed from the grass roots a new production plant including the reactive and purification sections to exploit it industrially.

Kinetic parameters for the reaction have been derived by regression of experimental literature data with a power law pseudo-homogeneous model and they were used for a preliminary sizing of the reactor. A shell&tube heat exchange reactor was implemented to control the exothermicity of the reaction, with simultaneous steam production and three catalyst layers (200, 500 and 2000 kg) with intercooling. 99.5% ethanol conversion and 84% selectivity to ethylene oxide were achieved, with ca. 100 kmol/h productivity, starting from the feedstock availability of a commercial bio-refinery.

The product is first recovered with an absorption column (releasing most N_2, CO, O_2 and CO_2 in gas phase, followed by a stripping column. A further distillation column separates crude ethylene oxide as distillate, while acetaldehyde, diethyl ether and minor impurities as bottom product.

Further purification options for ethylene oxide and for the recovery of by-products were also compared to generate different scenarios for the economic assessment of the plant.

Enabling technologies to boost cellulose selective valorisation over bifunctional catalyst

Giorgio Grillo,[a] Silvia Tabasso,[b] Federica Menegazzo,[c] Michela Signoretto,[c] Giancarlo Cravotto,[a] and Maela Manzoli[a]*

[a] *Department of Drug Science and Technology and NIS - Centre for Nanostructured Interfaces and Surfaces, University of Turin, Via Pietro Giuria 9, 10125, Turin, Italy;* [b] *Department of Chemistry, University of Turin, Via Pietro Giuria 7, 10125, Turin, Italy;* [c] *Department of Molecular Sciences and Nanosystem, Ca' Foscari University Venice and INSTM Consortium RU Ve, Via Torino 155, 30170 Venezia Mestre, Italy.*

The dependence on non-renewable resources, as well as the continuous energy demand are currently pushing the research toward alternative feedstocks, such as lignocellulosic biomass, to produce fuels and chemicals and abate the environmental impact. In this frame, residual lignocellulosic material could be used as the substrate for zero-waste cascade protocols into valuable chemicals, one of the hottest goals of current research. 5-hydroxymethylfurfural (HMF) derives from the conversion of cellulose through the dehydration of fructose. HMF is a key intermediate for the production of fine chemicals, such as 2,5-furandicarboxylic acid (polyester precursor), 2,5-dimethylfuran (potential biofuel), and gammavalerolactone, used as fuel additive and green solvent. [1] In particular, the conventional method to obtain 5-HMF involves the use of concentrated mineral acids (H_2SO_4, HCl and H_3PO_4) as catalysts at elevated temperature and pressure for hydrolyzing lignocellulosic building blocks such as glucose and fructose [2], or cellulose [3]. As a consequence, product decomposition, corrosion of the reactor along with the need of supplementary neutralization of acid reaction products contribute to enhance the process cost and the environmental impact.

Herein we report a sustainable HMF synthesis mediated by microwave (MW) irradiation, starting from microcrystalline cellulose, in the presence of simple heterogeneous acid catalysts. The focus of the work is the removal of strong acids by means of synergistic effects of lab made sulfated zirconia (ZS from 2 wt% to 8 wt%) and commercial zeolites (Y or β). In order to estabilish activity/acidity relationships, different conditions (time, temperature and catalyst loading) were screened. Furthermore, the effects of planetary ball-milling on the formation of a more reactive catalytic system as well as on the amorphisation of cellulose were investigated.

The optimized protocol improved the overall reaction (hydrolysis, isomerization and dehydration) leading to nearly complete conversion and high selectivity and yield in HMF in only one hour. N_2 physisorption at 77 K, DR UV-Vis spectroscopy, XRD and HRTEM combined with EDS probe were employed to obtain information on both substrate and catalyst, pre- and after-reaction. Complete characterization of the products was performed by GC-MS analysis.

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Green deep eutectic solvents and microwave technology towards a closed loop biorefinery

Silvia Tabasso,[1] Giorgio Grillo,[2] Emanuela Calcio Gaudino,[2] Roberto Rosa,[3] Cristina Leonelli,[4] Ana Timonina,[5] Saulius Grygiškis,[5] Giancarlo Cravotto[2]

[1]Dipartimento di Chimica, Università di Torino, Via P. Giuria 7, 10125 Torino; [2]Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino, Via P. Giuria 9, 10125 Torino; [3]Dipartimento di Scienze e Metodi dell'Ingegneria, Università degli Studi di Modena e Reggio Emilia, Via Amendola 2, 42122 Reggio Emilia;[4] Dipartimento di Ingegneria "Enzo Ferrari", Università degli Studi di Modena e Reggio Emilia, Via Vivarelli 10, 41125 Modena;[5] JSC Biocentras, LT-14117 Vilnius, Lithuania.

Owing to the increasing environmental concerns, biomass conversion to fuels and valuable platform chemicals has attracted remarkable attention over traditional petroleum-based industrial processes, according to a biorefinery approach. Currently, the most promising commercially viable route for lignocellulosic biomass valorisation is fermentation of cellulose and hemicellulose sugars into ethanol [1]. Indeed, being the conversion of lignocellulose to ethanol a complex and expensive process, the cost of bioethanol obtained cannot compete in the market. However, a promising strategy to lower the production cost of cellulosic ethanol is a biorefinery development, which entails the valorisation of all the components of biomass through the production of chemicals besides ethanol, according to a zero-waste approach. In this frame, a closed-loop biorefinery approach involving the combined use of biomass-derived solvents and enabling technologies could fulfil the sustainability criteria for future exploitation of renewable resources [2]. A novel biomass pretreatment combining natural deep eutectic solvents (NaDESs) and microwave (MW) technology was therefore developed [3], where microwaves can promote the selective activation of substrate thereby reducing the overall process time and energy consumption. The synergy between microwaves and NaDESs prompts an efficient biomass delignification due to the reduction of solvent viscosity and the consequent improved mass transfer resulting by the generation of high-energy microenvironments. This novel biomass pretreatment showed a high potential for lignin fractionation/recovery and sugar release in the following enzymatic hydrolysis. A new class of lignin derived NaDESs (LigDESs) was also investigated, showing promising effects in wheat straw delignification. To better understand the interaction of MW with these green solvents, the dielectric properties were also investigated. Furthermore, a NaDES using as hydrogen bond donor the lignin recovered after biomass pretreatment was prepared. This showed excellent dielectric properties and could be a promising solvent for a wide range of MW-assisted applications. This study enabled the full valorisation of all the biomass components, aiming to a circular loop of biorefinery processes.

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Microwave-assisted $FeCl_3$-catalysed production of glucose from giant reed and cardoon cellulose fraction and its fermentation to new generation oil by oleaginous yeasts

Nicola Di Fidio[a], Claudia Antonetti[a], Giorgio Ragaglini[b], Anna Maria Raspolli Galletti[a]

[a] Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124 Pisa, Italy; [b] Dipartimento di Scienze Agrarie e Ambientali - Produzione, Territorio, Agroenergia, University of Milan, Via Celoria 2, 20133 Milan, Italy.

The replacement of fossil fuels and materials with biofuels and bioproducts is a crucial current global goal. Biorefining of lignocellulosic biomass generates pentose and hexose sugars which can be converted into several added-value bio-based compounds. Among biofuels, biodiesel is one of the most promising renewable energy sources since it does not require new technology and engines for its use. Traditional biodiesel is produced on the industrial scale starting from vegetable oils obtained from oleaginous crops, such as palm oil, rapeseed oil and sunflower oil. However, most of the oleaginous plant species are food crops, determining the ethical debate on the right use of these renewable resources and the competition between the energy industry and food chain. An innovative and promising solution is represented by single cell oil (SCO) produced from oleaginous yeasts. This new generation oil, if obtained from low or negative value industrial waste, represents a promising platform chemical for the production of biodiesel, biosurfactants, animal feed and biobased plastics [1]. This study investigated the microwave-assisted $FeCl_3$-catalysed hydrolysis of giant reed (*Arundo donax* L.) and defatted cardoon (*Cynara cardunculus* L.) cellulose fractions to give glucose. Giant reed is a promising energy crops able to grow on marginal lands, while cardoon stalks are the crop residue in the production of vegetable oil. A preliminary acid pretreatment was adopted for giant reed [2], while steam-explosion pretreatment was performed on cardoon [3], both allowing a significant removal of xylan fractions. Under different reactions conditions, the microwave-assisted $FeCl_3$-catalysed hydrolysis converted the two pretreated feedstocks into glucose-rich hydrolysates which were employed as fermentation medium for the production of SCO by the oleaginous yeast *Lipomyces starkeyi* DSM 70296. For giant reed, the low production of furanic compounds enabled the direct fermentation of undetoxified hydrolysates, while for cardoon the furfural removal was necessary before the fermentation step. After hydrolysis, for both hydrolysates the fermentation provided promising lipid yields (~14 wt%) and oil content (~25 wt%). Figure 1 shows the process layout of the implemented third-generation biorefinery scheme. The SCO appears a valid candidate for the production of new generation biodiesel with good oxidative stability and cold flow properties. Moreover, it resulted very similar to palm and rapeseed oils, usually employed as a renewable source for the production of traditional biodiesel.

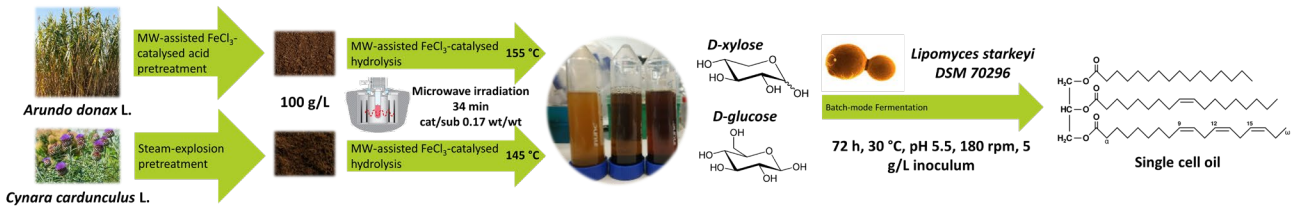

Figure 1. Schematic representation of the implemented biorefinery scheme.

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Theoretical study of glucose oxidation to glucaric acid using gold based catalyst

Alessia Ventimiglia[a], Ivan Rivalta[a], Eleonora Monti[a], Nikolaos Dimitratos[a], Marco Garavelli[a], Tommaso Tabanelli[a] and Fabrizio Cavani[a]

[a] Department of Industrial Chemistry "Toso Montanari", Alma Mater Studiorum – University of Bologna, Viale del Risorgimento, 4, 40136 Bologna, Italy

The glucaric acid (GLA) has been identified as a "top value-added chemical from biomass" [1] that can be employed for many uses; for instance, it could be a precursor of adipic acid, a monomer of Nylon-6,6. This process has the advantage of starting form glucose (GLU), renewable raw material, to obtain products of industrial interest, such as gluconic and glucaric acids. In recent years, in order to replace the current use of HNO_3 as a stoichiometric oxidant, new processes to obtain GLA in an economic and environmental sustainable way have been proposed: in particular, gold nanoparticles have been proved to act as oxidation catalyst for GLU oxidation in mild conditions. Our research is focused on the mechanism of oxidation of GLU to GLA that we routinely perform in our laboratory using molecular oxygen as oxidant agent and preformed colloidal gold nanoparticles supported on active carbons as catalysts in basic conditions (see Figure 1).

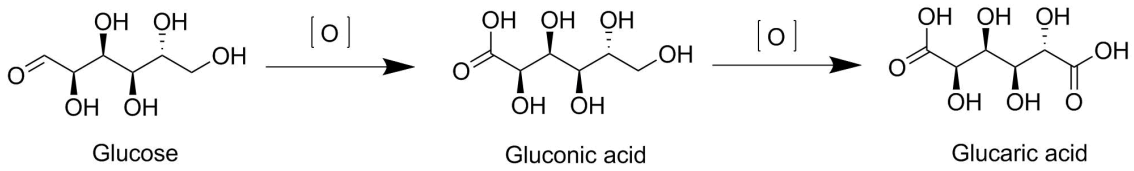

Figure 1: Glucose oxidation pathway towards glucaric acid via gluconic acid.

In order to obtain information on the catalytic mechanism at the atomistic level, we performed a computational study based on density functional theory (DFT) and atomistic modeling of the gold nano-catalyst. In particular, we have modelled both highly symmetric (i.e. icosahedral and cubo-octahedral [2]) and distorted Au_{55} nanoparticles [3] along with molecular cluster models of the Au(111) and Au(100) surfaces [4]. On these various models we have studied the adsorptions of various species involved in the catalysis, including OH species, GLU, GLA and potential intermediate species, like the gluconic acid, providing fundamental information on the catalytic mechanism and on deactivation phenomena.

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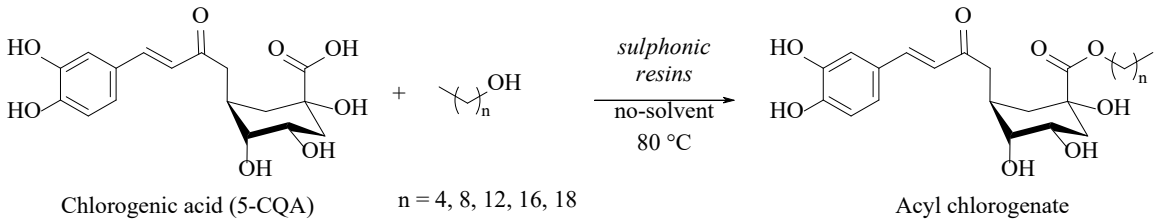
HETEROGENEOUS CATALYSIS IN THE ESTERIFICATION OF NATURAL ANTIOXIDANTS

Valeria Pappalardo, Federica Zaccheria, Nicoletta Ravasio

CNR SCITEC, Via Golgi 19, 20133 Milano

The valorization of agro-food industry residues is a pillar of circular economy. In the framework of project CirCo aiming at enhancing silverskin, a residue of the coffee roasting industry with almost no application, several products are under development. Among these, chlorogenic acid (CGA) [1], a natural polyphenol widespread in nature (plants, vegetables, fruits), displays several pharmacological and biological activities such as antioxidative, antibacterial, antihypertensive, antitumor, anti-inflammatory [2]. However, its highly hydrophilic structure strongly limits its bioavailability and hinders the use into oil-based products such as cosmetic and nutraceutical preparations.
To overcome this drawback, CGA can be lipophilized through esterification with a fatty alcohol [3]. The use of heterogeneous Brønsted solid acid catalysts, such as the sulphonic resins Amberlite® IR120 and Amberlyst® 15, resulted greatly effective in the direct acylation of CGA with fatty alcohols (4, 8, 12, 16, 18) in a sustainable, solvent free, one-pot reaction (Scheme 1).



Scheme 1

Butyl, octyl- and lauryl- chlorogenate were isolated in high yields (up to 93%) and fully characterized by NMR and LC-MS analyses. The antioxidant activity of these products has been studied and compared to unsubstituted CGA (Figure 1).
Preliminary reactions highlighted the applicability of this method also to the esterification of mono- and oligo-saccharides.

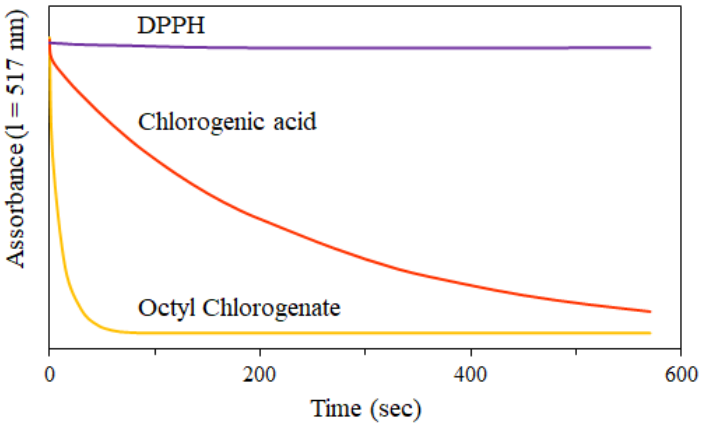


Figure 1

• **Acknowledgements** Cariplo Foundation and Innovhub, Grant 2017-0988 are acknowledged for funding.

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Amberlite IR120 as catalyst for the levulinic acid esterification reaction in batch and continuous operation

Carmelina Rossano [a], Vincenzo Russo [a], Rosa Vitiello [a], Rosa Turco [a], Riccardo Tesser [a], Martino Di Serio [a]

[a] *Chemical Science Department, University of Naples "Federico II", Via Cintia, I-80126-Naples, Italy*

Levulinic acid (LA) is an organic compound which has been replacing petroleum products becoming a versatile building block for a variety of high value-added chemicals, hence it was considered one of the most important platform chemicals. The acid catalyzed esterification of LA with alcohols produces levulinate esters (i.e., methyl, ethyl, propyl and so on) which can be used as fragrances, flavouring agents and fuel additives [1]. Esterification reactions are usually performed using homogeneous acids catalysts such as H_2SO_4, H_3PO_4 or HCl. Nowadays, they are replaced by heterogeneous catalysts that are preferable because are easily recovered and reused. Earlier studies [2-4] have established that the cation exchange resin Amberlite IR 120 for the reaction of LA with ethanol was revealed to be, among the different classes of catalysts (i.e., ion exchange resins, zeolites, sulfated metal oxides, silica), an active and affordable, green catalyst that can be use repeatedly without a significant decrease in its capacity. Since the kinetic study of ethyl levulinate is not yet reported in literature over Amberlite IR120, it was deeply investigated in the present work. Experiments were conducted firstly in a batch reactor evaluating the effect of operating conditions (i.e., temperature, stirring rate, reactants molar ratio and catalyst loading) and determining the kinetic constants, the rate constant and the activation energies. Successively, continuous esterification in a fixed bed reactor packed with the same catalyst was conducted and the kinetics was further validated. The collected experimental data were interpreted with a reliable model also considering the mass transfer phenomena involved in the reaction network.

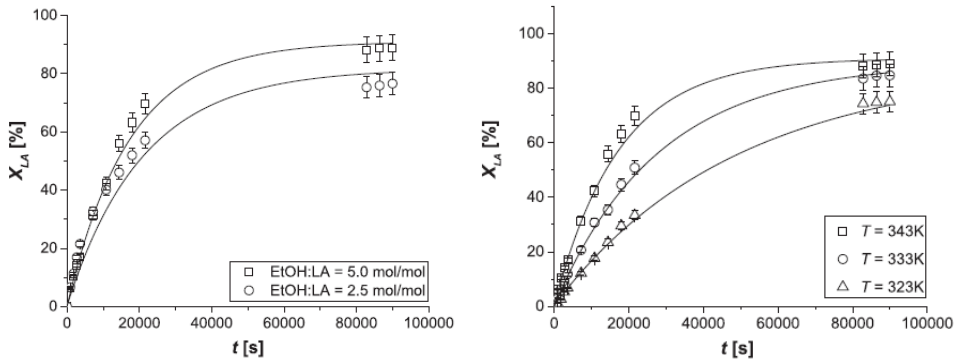

Figure 1. On the left, the effect of EtOH/LA ratio on the LA esterification fixing the temperature at 343 K. On the right, the effect of temperature fixing the EtOH/LA molar ratio of 5:1. Symbols are the experimental data, lines the calculated values.

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Synthesis of new biopolymers by biomasses valorization

Silvia Giorgi[a], Alice Cappitti[a], Roberto Giannelli[a], Antonella Salvini[a]

[a]Department of Chemistry "Ugo Schiff" University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (Italy)

The lignocellulosic biomasses valorization, as raw materials to industrial production, allows solving the problems related to agri-food and forest wastes [1]. Moreover, the growing attention to environmental problems has increased interest to reduce the consumption of fossil resources and at the same time to enhance waste disposal without changing the availability of natural resources used as food.
In this context glucose, which can be obtained from lignocellulosic wastes, is a versatile building block to produce several innovative biopolymers. The use of derivatives of natural substances can allow obtaining products that are biocompatible, biodegradable, cheap and with high stability.
In this work, two different strategies were used to protect the anomeric position of glucose for its use in further syntheses.

In the first synthetic strategy, the methyl D-glucopyranoside was synthesized by methylation of the anomeric position, both directly from D-glucose and starting from polysaccharides as cellobiose, starch and pullulan (an oligosaccharide material derived from the enzymatic transformation of starch [2]) by cleavage of the glycosidic bond. In fact, the glycosylation reaction, exploiting the reactivity of the hemiacetal group and using heterogeneous catalysts, allows the insertion of alcohols with different structural features, avoiding the protection-deprotection steps. Afterward, the methyl D-glucopyranoside was used to obtain molecules by a transesterification reaction with ethyl methacrylate. Then, the monomer obtained was used to synthesize new biopolymers through radical polymerization reactions and in particular the homopolymer and several copolymers, with ethyl methacrylate and vinyl acetate in a different molar ratio between the two monomers, were synthesized.

Following the second strategy, the glycosylation reaction was used to introduce an alkenyl group in an anomeric position by reacting glucose with 3-buten-1-ol. Also starting from this monomer, new biopolymers have been obtained.
For all these products, suitable synthetic procedures were designed and used to obtain copolymers with high purity and avoiding protection/deprotection steps in agreement with the principles of green chemistry and industrial sustainability.
All the monomers and copolymers were characterized using FT-IR and NMR spectroscopies, while thermoanalytical technique was also employed for polymers.
The synthesized biopolymers showed different solubility and properties, resulting suitable for their use in different application fields; in particular, they could be interesting also in the field of science of conservation of cultural heritage because these products have a low environmental impact, and they have affinity and compatibility for the cellulosic materials which constitute some works of art (i.e. wood, paper).

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Innovative heterogeneous catalysts for the reduction of levulinic acid derivatives to γ-valerolactone and consecutive reduction products

Riccardo Bacchiocchi[a], *Tommaso Tabanelli*[a], *Daniele Bianchi*[b] *and Fabrizio Cavani*[a]

[a] *Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy;* [b] *Istituto Eni Donegani, Via Fauser 4, 28100 Novara, Italy*

Levulinic acid (LA) and its esters (e.g. methyl levulinate, ML) are polyfunctional molecules that can be obtained directly from lignocellulosic biomass by hydrolysis or alcoholysis respectively[1]. Due to its potentials as chemical intermediate, LA has been classified as one of the top 12 building block chemicals by the United States Department of Energy[2]. In particular, the most investigated strategy for LA valorization is its hydrogenation toward valuable compounds such as fuel additives, solvents and other added-value chemicals. Most of the published manuscripts on this topic mainly focused on the conversion of LA to γ-valerolactone (GVL) using relatively high pressure of H_2. However, few studies in literature report on the production of consecutive reduction products, namely 2-methyltetrahydrofuran (2-MTHF), 1,4-pentadiol (1,4-PDO)[3], valeric acid (VA) and its ester (e.g. methyl valerate, MV)[4]. In this context, the use of noble metal catalysts supported over acid supports (e.g. zeolites) is reported as a suitable strategy in order to promote GVL over reduction to VA or its esters[4]. For all these reasons, the catalytic activity of a 3wt% Rh/H-ZSM-5 for the hydrogenation of LA or ML has been investigated. **Fig. 1** shows the results in terms of ML conversion, GVL yield, MV+VA yield and carbon balance (expressed as yield sum/conversion ratio, Y/C) in function of the reaction temperature. Increasing the reaction temperature caused an increase of MV+VA yield with a concomitant decrease in GVL yield. Interestingly, Rh/H-ZSM-5 shows high selectivity in valerates (MV and VA). This is mainly due to the strong acidity of the support which promote the ring-opening hydrogenolysis of GVL, usually identified in literature as the rate determining step. The reaction mechanism was investigated starting from intermediates and products under same reaction conditions. Differently, Re is known for its oxyphilic nature and has been recently reported in literature for promoting the selective hydrogenation of carboxylic acids[5]. Therefore, a different strategy has been investigated by preparing a bimetallic system supported over silica (i.e. 4wt%Rh4wt%Re/SiO_2). Interestingly, this material shows that is possible to reduce GVL, obtaining 2-MTHF as main product. In conclusion, these preliminary results demonstrate the enhanced catalytic activity of Rh/H-ZSM-5 in promoting the consecutive reduction of GVL to valeric acid and its esters. A completely different behavior was observed using Re-based catalyst, which promotes the selective hydrogenation of carboxylic group. In the near future more efforts will be directed toward the synthesis of Re-based bimetallic catalysts supported on zeolites (e.g. RhRe/H-ZSM-5) with the aim of further improve the catalytic activity and the production of consecutive reduction products, like pentanol.

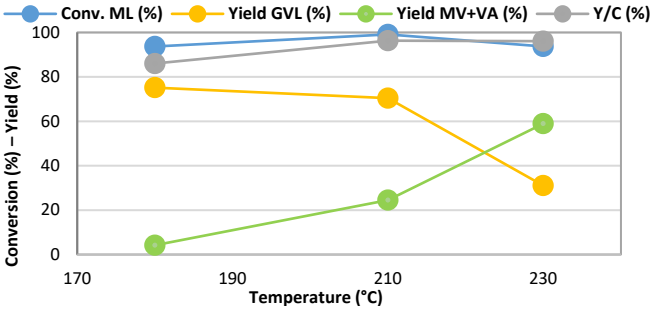

Fig. 1 Reaction condition: Solvent free, P_{H2} = 40 bar; time = 4 h m_{cat} = 5wt% of **Rh/H-ZSM-5**

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Hydrogenolysis of aromatic ethers under lignin-first conditions

Emilia Paone,[a] Amerigo Beneduci,[b] Giuseppina Anna Corrente,[b] Angela Malara,[a] Francesco Mauriello [a]

[a] Dipartimento di Ingegneria Civile, dell'Energia, dell'Ambiente e Dei Materiali (DICEAM), Università Mediterranea di Reggio Calabria, Via Graziella, Loc. Feo di Vito, I-89124 Reggio Calabria, Italy; [b] Dipartimento di Chimica e Tecnologie Chimiche (CTC), Università della Calabria, via Pietro Bucci, I-87036 Arcavacata di Rende, Italy

Owing to the improvement of reductive catalytic fractionalization (RCF) processes (also known as lignin-first biorefinery) [1], a complete valorization of lignocellulosic biomasses into value-added chemicals, renewable energy and biofuels is firmly established today.
The basic catalysis beyond the depolymerization of lignin in RCF processes involves the lysis of C–O and C–C bonds in the presence or in the absence of added molecular hydrogen by using simple C1-C3 alcoholic H-donor solvents (methanol, ethanol and 2-propanol) as such or in mixture with water in the temperature range of 120–240 °C.
In this contribution we aim to investigate the molecular catalysis occurring in the lignin-first upgrading of lignocellulosic biomasses, by using commercially available Ru/C and Pd/C catalysts for the C–O bond cleavage of three lignin model aromatic ethers (DPE, PPE and BPE) [2]. A detailed study on the H-donor source as well as on the effect of the water content in water/organic mixture solvent media on the conversion of aromatic ethers and in driving the products selectivity is also presented.
Ru/C was found to be a better catalytic system, with respect to Pd/C, in the production of aromatic compounds from lignin model diphenyl ether (DPE) that was studied as model molecule to investigate the complex hydrogenolysis-hydrogenation-hydrolysis reactions that occur in the cleavage of the etheric 4–O–5 C–O bond.
The direct hydrogenolysis is preferred in the presence of 2-propanol (that provides best results both in terms of DPE conversion as well as in the production of aromatic compounds), whereas the hydrogenation-hydrogenolysis pathway is favored by using molecular hydrogen. At the same time, by adding water as co-solvent, the impact of the reductive hydrolysis becomes more significant allowing the preferential formation of hydrogenated phenolic compounds.
Noteworthy, a very high selectivity to the hydrogenolysis was observed in the case BPE and PPE as a consequence of both their higher steric hindrance, with respect to DPE, that limits the adsorption of their aromatic rings onto the Ru metal surface as well as to the lower tendency of phenol to undergo a hydrogenation process when toluene or ethyl benzene are present in the reaction medium.

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Experimental study of interactions between biomass pellets and oxygen carriers for chemical looping gasification in fluidized beds

Stefania Lucantonio [a], Andrea Di Giuliano [a], Barbara Malsegna[a], Katia Gallucci [a]

[a] Department of Industrial and Information Engineering and Economics (DIIIE), University of L'Aquila, Piazzale E. Pontieri 1-loc. Monteluco di Roio, 67100 L'Aquila, Italy

This work is part of the ongoing European research project Horizon 2020 CLARA (Chemical Looping Gasification for Sustainable Production of Biofuels, Grant Agreement n.817841), focused on advancing the innovative technologies of the devised biomass-to-liquid process chain [1], with University of L'Aquila as one of the thirteen international partners of the project. The goal of CLARA is to develop and investigate the feasibility of biofuel production from syngas produced by Chemical Looping Gasification (CLG) of residual biomass by means of oxygen carriers (OCs) in dual circulating fluidized beds. OCs, thanks to their redox properties, replace the oxidizing agents used in conventional gasification or combustion processes. In the complex framework of CLARA project, this experimental research work aims to study the behavior of biomass pellets during devolatilizations at different temperatures (700°C, 800°C and 900°C), in fluidized beds made up of OCs. The investigation involved 14 kinds of biomass (raw pine and wheat straw pellets, or wheat straw pellets pre-treated by torrefaction, washing, addition of minerals) and 4 fluidized bed materials (3 OCs and sand as a reference). Tests were performed by a laboratory scale quartz reactor (5 cm internal diameter). N_2 was used as fluidizing gas, as it is inert, at 1.5 times the minimum fluidization velocity of the investigated bed material so to ensure similar fluid-dynamic conditions for all tests. Three repetitions were carried out for each set "biomass/temperature/bed material", totalizing 504 devolatilizations.

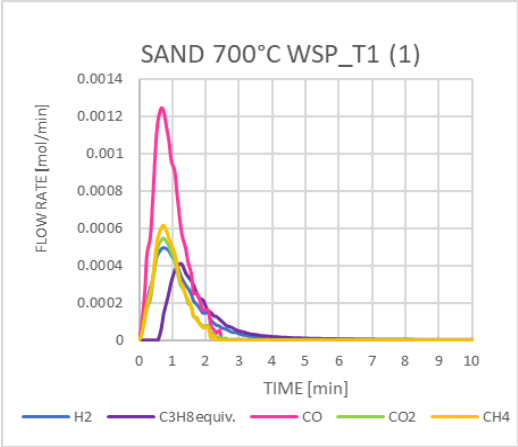

Figure 1: Flow rates of dry syngas components during the devolatilization of one pellet of raw wheat straw at 700 °C in a sand fluidized bed.

The composition of dried produced syngas was recorded on-line (0.2 Hz sampling rate) as volume percentages of H_2, CO, CO_2, CH_4 and hydrocarbons (cumulative equivalent C_3H_8 ppm). Related molar flow rates were calculated under the assumption of N_2 as the internal standard; Figure 1 represents one of the devolatilization tests in terms of these flow rates.

Some parameters (integral-averages) were calculated on the basis of these flow rates, to compare the behaviors of the different sets "biomass/temperature/bed material": 1) H_2/CO molar ratio; 2) carbon conversion; 3) gas yield; 4) gas composition.

This work showed that the temperature increase has a positive influence on syngas production and quality; it was also shown that the use of ilmenite OC and the torrefaction of biomasses improve the H_2/CO molar ratio of residual biomasses of 13.9%, 24.5% and 30.9% at 250°C, 260°C, and 270°C level of torrefaction temperature, respectively.

By combining the conclusions of this work with those from studies on pressure fluctuation signals made for CLARA by our research team [2], the most promising biomass-oxygen carrier-temperature combination were selected, for investigations at higher scales.

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Electrodes and electrolytes for aqueous dye-sensitized solar cells

Lucia Fagiolari[a], Matteo Bonomo[b], Simone Galliano[b], Guido Viscardi[b], Claudia Barolo[b], Federico Bella[a]

[a] *Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 - Torino, Italy;*
[b] *Department of Chemistry, Università degli Studi di Torino, Via Pietro Giuria 7, 10125 - Torino, Italy.*

Photovoltaic (PV) technology has evolved rapidly in the past few decades and now encompasses a large variety of materials and device structures. A key aspect to be considered in any PV technology is the operational durability under real outdoor conditions, as well as the sustainability of materials/components and the facile integration with energy storage systems.
In the last five years, dye-sensitized solar cells (DSSCs) with water-based electrolytes have been considered as one of the possible breakthroughs towards DSSCs large-scale diffusion. If opportunely developed and optimized, aqueous solar cells can be truly considered as zero-impact photovoltaic devices fabricated with non-toxic components [1,2,3,4].
We show here the possibility of jellying the electrolyte into a solid matrix to boost stability, the possible use of different redox mediators solvated by water, the formulation of TiO_2 pastes for screen-printable photoanodes operating in water, and the replacement of Pt cathodes with more sustainable alternatives.
Overall, we will show how much water-based photovoltaics represents a challenging topic in the current energy scenario, and how it will be able to provide safe, sustainable and easily processable solar cells for building-integrated photovoltaics and portable electronics.

Politecnico di Torino is gratefully acknowledged by F.B. and L.F. for granting the fund named "Contributo ERC per chi ha superato il primo step di valutazione"

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Carbon Dioxide Absorption Mechanism in Biocompatible Ionic Liquids Solutions

Francesca Rosso[a], Matteo Signorile[a], Giulio Latini[b,c], Sergio Bocchini[c], Candido Fabrizio Pirri[b,c], Francesca Bonino[a], Valentina Crocellà[a], Silvia Bordiga[a]

[a] Department of Chemistry, NIS and INSTM Reference Centre, Università di Torino, Via G. Quarello 15, 10135 and Via P. Giuria 7, 10125, Torino, Italy; [b] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10128, Turin, Italy; [c] Center for Sustainable Future Technologies – Istituto Italiano di Tecnologia, via Livorno, 60, 10144, Torino, Italy

The rise of the average world temperature, due to anthropogenic carbon dioxide (CO_2) emissions, resulted in the need of an efficient and sustainable carbon capture approach. For this purpose, the substitution of amine scrubbing with CO_2 bubbling in dimethyl sulfoxide (DMSO) solutions of non-toxic ionic liquids (ILs) can be a valuable alternative, as described in previous works. [1, 2] ILs composed by choline as the cation and amino acids as anions, diluted in DMSO (B_p = 189°C) have been proved to be effective CO_2 absorbents and to show full CO_2 release at low temperature (80°C), avoiding the solvent vaporization. [1] The amino acids amine functional group can react with CO_2 according to 1:1 stoichiometry, leading to the formation of carbamic acid, or 2:1, forming ammonium carbamate.

The aim of the present work is to investigate (i) the effect of the CO_2 concentration in the flue gas on the absorption kinetic, (ii) the effect of the IL concentration in DMSO solutions on the reaction mechanism among CO_2 and IL and (iii) the relationship between the CO_2 absorption performance and the reaction mechanism occurring in the presence of different amino acids. Based on preliminary studies [3] (whose results are briefly reported in Figure 1), glycinate and sarcosinate have been selected as the most interesting amino acid anions.

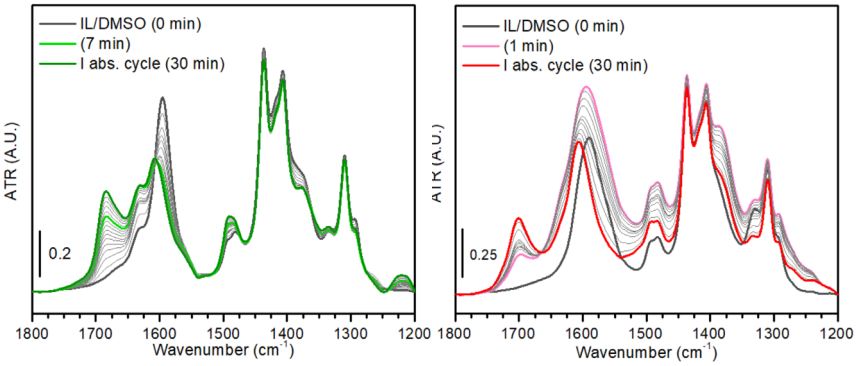

Figure 1: IR spectra of CO_2 absorption (20% v/v of CO_2 in N_2) by sarcosine (green) and glycine (red) containing ILs, at 12.5% w/w of IL in DMSO.

The effect of the CO_2 concentration in the flue gas was studied by employing gravimetric methods (to quantify the amount of CO_2 absorbed), whereas the reaction mechanism was examined by means of vibrational spectroscopic measurements, under *in situ* conditions, and DFT calculations. Different reaction mechanisms in the presence of a primary amine moiety (glycine) and a secondary amine (sarcosine) have been investigated also by using DFT. Calculation results provided the energetic profiles for the aforementioned CO_2-IL reactions and allow predicting infrared spectra, thus facilitating the interpretation of experimental results.

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"*To Dissipate or not to Dissipate extra-Heat? This Is the Question!*" How to Reduce Energy Wastes in a Challenging Process at the Heart of P*2*G Chain

Lai Truog-Phuoc,[a] *Cuong Pham-Huu,*[a] Giulia Tuci,[b] Andrea Rossin[b] and Giuliano Giambastiani[a,b]

[a] *Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), UMR 7515 CNRS-University of Strasbourg (UdS), 25, rue Becquerel, 67087 Strasbourg Cedex 02, France.* giambastiani@unistra.fr

[b] *Institute of Chemistry of OrganoMetallic Compounds, ICCOM-CNR and Consorzio INSTM, Via Madonna del Piano, 10 – 50019, Sesto F.no, Florence, Italy.* giuliano.giambastiani@iccom.cnr.it

A challenging task of modern catalysis is to get cheap and robust catalytic materials based on non-critical components while ensuring at the same time energy-saving reactors schemes. This contribution describes Ni-loaded hybrids (N-doped Carbon Nanotubes supported)[1] and fully inorganic (γ-Al_2O_3 supported)[2] composites prepared to catalyze a highly exothermic process at the heart of the Power-to-Gas (P2G) chain: CO_2 methanation.

We demonstrated that a rational approach to the design and synthesis of Ni-based catalysts coupled with a conceptually new and energy-efficient handling of the extra-heat produced during the process lead to a highly efficient CO_2 methanation protocol for the production of Synthetic Natural Gas (SNG).

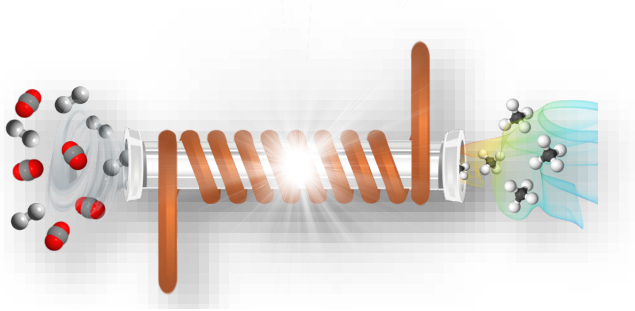

Figure 1. *Radiofrequency promoted CO_2 methanation*

The transition from a classical heating set-up (conduction/convection/radiation) to a "cold-reactor" [3] scheme based on the radiofrequency heating (Figure 1) of the Ni-active sites directly at the catalytic bed, boosts the catalytic process to the bounds of its inherent kinetic.[3] Accordingly, the reaction is efficiently carried out (X_{CO2} up to 98% with > 99% S_{CH4}) at temperatures (150-230 °C) much lower than those commonly claimed for related systems in the literature, hence ensuring an ideal energy balance to the net-zero decarbonization process.[2,3]

Acknowledgements. The TRAINER project (Catalysts for Transition to Renewable Energy Future) of the "Make our Planet Great Again" program (Ref. ANR-17-MPGA-0017) and the PRIN 2017 Project Multi-e (20179337R7) "Multielectron transfer for the conversion of small molecules: an enabling technology for the chemical use of renewable energy" are acknowledged for support to this work.

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A study of Kraft lignin conversion and possible upgrading to valuable compounds

Matteo Borella [a], Alessandro Alberto Casazza [a], Paola Riani [b,c] Gabriella Garbarino [a,c], Guido Busca [a,c]

[a] Department of Civil, Chemical and Environmental Engineering (DICCA), University of Genova, Via all'Opera Pia 15, 16145, Genova, Italy [b] Department of Chemistry and Industrial Chemistry (DICCI), University of Genova, Via Dodecaneso 31, 16145, Genova, Italy [c] INSTM, UdR Genova, Via Dodecaneso 31, 16146, Genova, Italy

Over the last century, world's population and energy demand[1] have increased by ruling out the need to find valid renewable alternatives for energy and chemical intermediate production[2]. Lignocellulosic biomasses represent a promising feedstock for biofuels and high value chemicals. As well-known, lignin, together with cellulose and hemicellulose, is one of the main components of lignocellulosic biomasses[3] but lignin viable applications are still limited[4]. Lignin is a complex aromatic-rich polymer, but its structure is strongly affected by the solvents that are adopted during the isolation procedure[5–7].

In this work, commercial lignin obtained from Kraft process (StoraEnso®, Lineo™ Classic Lignin, Kotka, Finland) has been used by investigating possible application. According to the literature, the isolation process of kraft lignin is performed using sodium sulfide, thus consistent sulfur amounts are expected in the final product (i.e., 2-4 wt.% depending on the feedstock)[5]. In this work, pyrolysis has been carried out at different temperatures (250°C to 550°C) in an inert atmosphere and in optimized reaction conditions[8, 9]. The distribution and composition of solid carbon residue, liquid condensed vapors and gases produced have been deeply characterized. At low temperature, the solid residue is the main fraction (80-90 wt.%) even though an increase in both gas and liquid is observed for reaction carried out at high temperature, achieving a liquid yield of 30 wt.% at 550°C. The liquid de-mixes in two different phases: one aqueous lighter phase, and a heavier phase mainly constituted by phenolic-like compounds produced by the cracking of the lignin polymer. The organic fraction has been separated using $CHCl_3$ as solvent. Then, MeOH/H_2O and alkaline H_2O extraction have been carried out, to efficiently separate different phenolic compounds.

Preliminary data have been also obtained regarding sulfur removal, that might affect the quality of the produced gas. Interestingly, several S-containing products i.e., H_2S, CH_3SH, CH_3SCH_3, CS_2 and SO_2 (GC-MS analysis) are found in the produced pyrolysis gas and their distribution changes as a function of the temperature and reaction conditions. In general, hydrogen sulfide was the main detected product. Following these results, an innovative reactor configuration has been outlined in order to purify the gaseous stream, thus attempting to achieve suitable purity and sulfur removal from the liquid and solid fractions. Several analyses are still undergoing to estimate the amount of sulfur removed.

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Multifunctional Hardening Accelerator for Low-Clinker Binders

Gilberto Artioli[2], Anna Bravo[1], Alberto Brocchi[1], Fabio Castiglioni[1], Maria Chiara Dalconi[2], Mikaela Decio[1], Giorgio Ferrari[1], Marco Mazzetti[1], Luca Torelli[1], Davide Salvioni[1], Luca Valentini[2]

[1]Mapei S.p.A., Via Cafiero 22, 20158, Milan (Italy);[2]University of Padua, Department of Geoscience, CIRCe Center, Via Gradenigo 6, 35131, Padua (Italy)

Each year, more than 4 billion tons of cement are produced worldwide, contributing for around 8% of global CO2 emissions. To bring the cement sector in line with the Paris Agreement on climate change, its annual emissions must fall by at least 16% by 2030 [1]. Clinker substitution with Supplementary Cementitious Materials (SCMs) such as fly ash, blast furnace slag, pozzolana, limestone and calcined clay is considered one of the most promising ways to reduce cement carbon footprint, as it can be done without investments in new equipment or changes in concrete processing [2]. However, SCMs generally react slower with water compared to clinker and this reflects on the strength development of concretes produced with blended cements. Many SCMs show enhanced reactivity when properly activated with strong bases (Alkali-Activated Materials, AAMs), such as NaOH and Na2SiO3 [3], but the use of such highly alkaline substances poses safety and environmental issues. For all these reasons, there is an urgent need for new admixtures able to activate SCMs. We developed a novel Multifunctional Hardening Accelerator (MHA) that works, at the same time, a) as an accelerator for the clinker phase via secondary nucleation promotion, b) as an activator for AAMs and c) as enhancer for the pozzolanic reaction. The new product is obtained from the controlled hydration of Portland cement in presence of excess water and a polycarboxylate ether (PCE) superplasticizer and consists of an alkaline suspension of micro-sized particles of nanostructured calcium silicate hydrate CSH nuclei, amorphous portlandite and AFm phases embedded in a polymeric matrix. The structure and the mechanism of action of the new product on various blended cements have been investigated by Environmental Scanning Electron Microscopy, X-ray Powder Diffraction, Thermal Analysis and Isothermal Calorimetry and the improved strength development imparted by MHA was studied by compressive strength measurements on mortar prisms. The new product is fully compatible with PCE superplasticizers and can be used to produce alkali-activated concretes characterized by high early-age strength and reduced carbon impact.

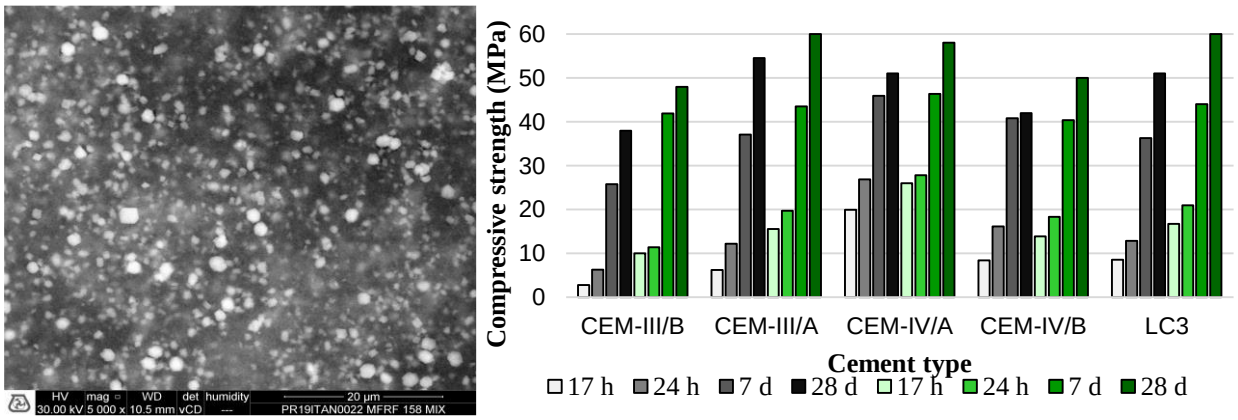

***Figure 1. Left** – ESEM image of the new product MHA; **Right** – Compressive strength at increasing curing time of mortars prepared with different binders without MHA (grey columns) and with 10% by weight of binder of MHA (green columns).*

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Optimization of HASE polymers effect in formulation of cement using Design of Experiment

R. Vitiello[a], P. Perrotta[a], R. Turco[a], V. Russo[a], M. Di Serio[a], R. Tesser[a]

[a]University of Naples Federico II, Department of Chemical Sciences, Complesso Universitario di Monte Sant'Angelo, 80126 Naples, Italy

The associative polymers HASE (Hydrophobic Alkali Swellable Emulsions) are a class of polymers having a comb architecture with hydrophobic groups randomly distributed along the backbone of the polyelectrolyte [1].They are used as rheological modifiers in formulations of paints and paper coatings, as they have a high thickening capacity, in fact low concentrations of HASE are enough to increase the viscosity of the solution by several orders of magnitude. Another use reported in the patent literature is that of superplasticizers for concrete [2].
In this work the synthesis of HASE to be used as superplasticizers in concrete was studied.
HASE polymers are generally obtained from the copolymerization in emulsion of methacrylic acid (MAA), ethyl methacrylate (EA) and an associative monomer (AM) in different ratios depending on the final uses. Associative monomers are compounds consisting of a poly (oxyethylene) chain linked to an alkyl (hydrophobic) group at one end and a polymerizable vinyl group at the other. When the associative monomer is copolymerized with methacrylic acid and ethyl methacrylate, the resulting polymer has a backbone consisting of MAA, EA and the vinyl group residue of the associative macromonomer, as well as flexible, water-soluble side chains that are terminated by a linear hydrophobic alkyl group [3].
In aqueous media the hydrophobic groups dynamically associate, leading to the formation of a transient or reversible network, which is the basis of the peculiar behavior of HASE [4]. In this work a solution of poly (ethylene glycol) behenyl ether methacrylate was used as an associative monomer (AM) which is characterized by a hydrophobic group of 22 carbon atoms and a polyethylene glycol chain of 26 units.
The DoE (Design of Experiment) statistical approach was used to verify the best ratio between the reagents and the best operating conditions in the synthesis of HASE polymers to be used as concrete superplasticizers, which allows to reach the set objective through the evaluation of all the variables considered significant that influence the final answer. In this case, the goal is to maximize the flare diameter of the cement mass, a parameter linked to fluidity, by means of the Flow Table Tests performed according to the ASTM C1437 standard [5]. A complete factorial design was adopted with 4 factors (continuous variables) studied on 2 levels, in such a way as to have 24 total combinations, to which a central experiment was added. Following the planning of the synthesis experiments and their execution, the performance data of the 17 samples in the fluidification of the cement were collected. The data were processed through a polynomial model in order to identify the optimal synthesis conditions. The design provided 2 optimal combinations (performance of the synthesized HASEs comparable to that of a commercial superplasticizer).

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Are Aqueous Hydrogen Peroxide and Sodium Percarbonate Efficient in the Inactivation of SARS-CoV-2?

Davide Mileto[a], Alessandro Mancon[a], Miriam Cutrera[a], Anna Gigantiello[a], Stefano Econdi[b,c], Maria Rita Gismondo[a], Matteo Guidotti[c]

[a] Laboratory of Clinical Microbiology, Virology and Bioemergency, ASST Fatebenefratelli Sacco, University Hospital L. Sacco, Milan; [b] University of Milan; [c] CNR-SCITEC.

To date, the most widely adopted methods to inactivate SARS-CoV-2 coronavirus on surfaces rely on concentrated aqueous alcohol solutions (>70%), hypochlorite-containing formulations and quaternary ammonium cationic surfactants. None of these virucidal formulations is free from drawbacks [1]. Thus, a biocidal agent that is fast-acting, chlorine-free, intrinsically safe (in terms of flammability and toxicity to humans and environment), chemically stable, and cheap would be a reliable alternative countermeasure against SARS-CoV-2.

In the present work, the effectiveness of aqueous H_2O_2 solutions was evaluated in the inactivation of SARS-CoV-2, controlling concentration, pH, and additives. Two different aqueous H_2O_2 concentrations were tested: 3 wt.%, as found in common household disinfectants, and 0.5% w/w, as described in previous reports [2]. The commercially available adduct sodium percarbonate, $Na_2CO_3 \cdot 1.5H_2O_2$ was also tested for its high stability and robustness over time, when in dry form, being suitable to efficiently replace unstable aqueous H_2O_2 solutions. The B.1 and B.1.351 (so-called South Africa variant) viral lineages were used.

Under acidic conditions and thanks to the addition of simple co-formulants, H_2O_2 is an active ingredient for the inactivation of SARS-CoV-2 virus. The co-presence of citric acid to obtain an acid pH and a minimum contact time of 5 min was effective to achieve a very good virus depletion with >4 $\log_{10}$ diminution with B.1 virus [3]. Such a result is the best performance recorded so far in the field of virus inactivation with diluted aqueous H_2O_2 solutions (Figure 1). Sodium percarbonate showed a less rapid inactivation capability, but in 15 min, a satisfactory reduction of more than 3 orders of magnitude in virus titer was attained. The effectiveness of the H_2O_2 + citric acid solution was confirmed also on South Africa variant strain, with a 4 $\log_{10}$ viral titer reduction after 15 min.

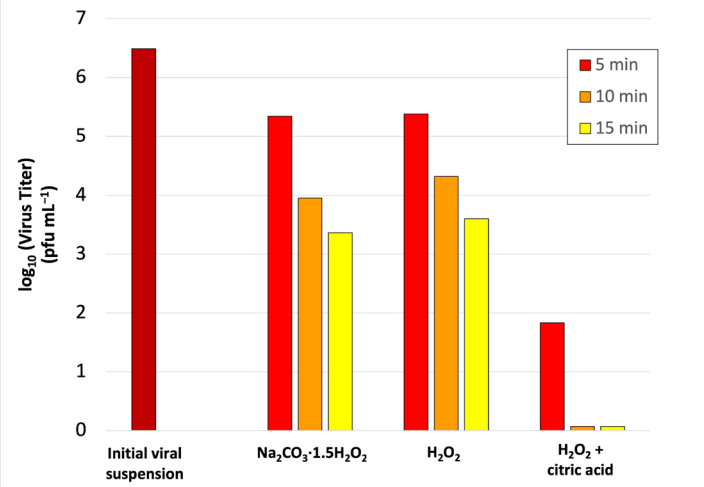

Figure 1. Inactivation performance against SARS-CoV-2 of H_2O_2-containing solutions under various conditions

Acidified diluted H_2O_2 solutions proved to be easily accessible, cheap, safe, robust, environmentally friendly, and efficient disinfecting agents, also against clinically relevant South Africa variant[4], for everyday-life sanitization practices to be used by non-specialized personnel too. Moreover, such a formulation may represent a viable and sustainable approach to obtain reliable virucidal solutions for a very broad range of the world population, also in countries with weaker economies.

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Chemical Plants Active Learning by Virtual Immersive Laboratory: the Eye4edu Project

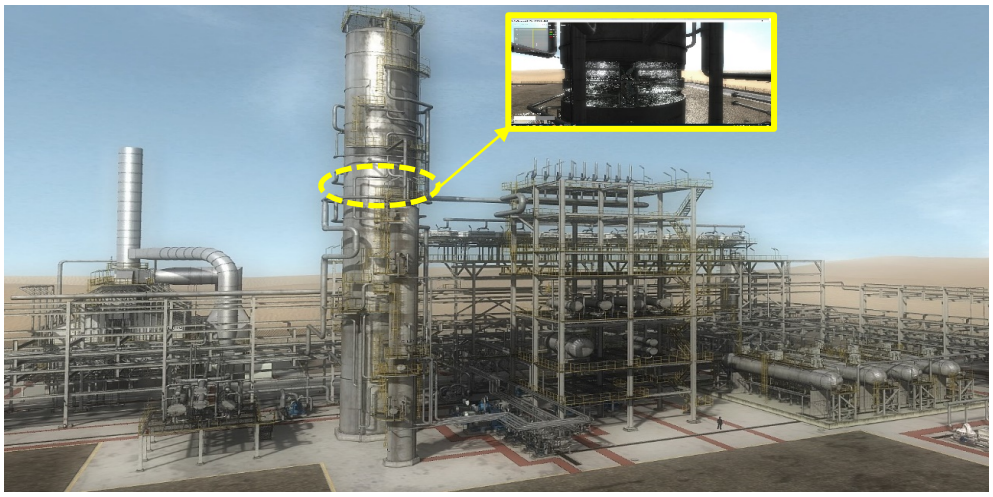
Carlo Pirola

[a] *Università degli Studi di Milano, Dipartimento di Chimica, via Golgi, 19 – 20133 Milano (Italy)*

Virtual immersive laboratories represent a new and appealing tool for education in science, technology and engineering degree courses, complementary to experimental activities performed in laboratory or exercises performed in traditional rooms. The dynamic simulation of chemical plants coupled with their 3D CAD physical visualization opens the possibility to have at disposal very realistic representations of industrial processes, suitable to be used for visit and exercises in virtual chemical laboratories. In the University of Milano, a new educational project called Eye4edu [1], proposed different exercises on a virtual immersive Crude Distillation Unit (VCDU), with the aim to apply an active learning scenario for the learning of the structure of the single unit operations, the plant in general and the control and intervention operating procedures. The project was proposed to the bachelor and master students for the degree in Industrial Chemistry in the Milan university in the years 2019-2021.

VCDU is based on the combination of the actions of "AVEVA XR for Training", formerly EYESIM, for the physical representation of the plant structure and DYNSIM software for the simulation of the dynamic chemical behavior (thermodynamics, physico-chemical properties, fluid-phase equilibria, transport phenomena) of the plant. Both the software have been developed by AVEVA Company.

Several exercises on the VCDU were proposed to the students both for practical and management operations in the plants. The students were required to work on the basis of the information available in the technical documents as PFD and P&ID. The project was proposed both in the presence and as distance learning, respectively before and during the health emergency due to SARS-CoV-2 pandemic. The description of the virtual laboratory and an analysis of its use and educational impact in face-to-face and remote delivery is reported in this contribution.



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Manganese- and cobalt-based catalysts for homogeneous hydrogenations

Veronica Papa,[a,b] *Kathrin Junge,*[b] *Matthias Beller*[b]

[a] *Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy;* [b] *Leibniz-Institut für Katalyse e. V., Albert-Einstein-Straße 29a, 18059 Rostock, Germany*

Catalysis is one of the major chemistry subjects in academic and industrial research and many efforts are made by the scientific community in the design and investigation of new catalytic systems. Catalysis is one of the chemical fields that clearly represent the concept of sustainability; therefore, it is not surprising that huge investments are constantly made in this field both from the economical and the scientific point of view.
Traditionally, in homogeneous catalysis the use of noble metal complexes dominated this field. Nowadays, there is an increasing interest from researchers to develop molecularly-defined catalysts based on non-noble metals. These are considerably lower in price than noble metals and in general they are also "biocompatible" because they are involved in biochemical processes, have acceptable environmental impact and, in some cases, are less toxic than noble metal alternatives.
In this regard, our goal was to explore the activity of novel non-noble metal-based catalytic systems in redox transformations of industrial relevance, such as homogeneous reduction of several unsaturated organic substrates by molecular hydrogen. A new class of NNP pincer ligands has been synthesised and coordinated to a manganese (I) metal centre. These complexes have been tested in hydrogenation reactions and their catalytic performance is remarkable for challenging substrates such as amides[1] and *N*-heterocycles. Additionally, the hydrogenation of amides was studied in depth using an *in situ* formed cobalt catalyst in the presence of the tridentate phosphine Triphos.[2] Using the NNP-Mn(I) pincer complexes results in the hydrogenolysis of amides to the corresponding alcohols and amines via a C–N bond breaking pathway. On the other hand, using the Co/Triphos system, it is possible to tune the selectivity towards a C–O bond cleavage pathway, obtaining an amine as the major product. Concerning the hydrogenation of *N*-heterocycles, not only the catalytic activity of the NNP-Mn pincer complexes was investigated but also the one of the simple, readily available Mn pentacarbonyl bromide,[3] thus paving the way to ligand- and additive-free homogeneous catalytic hydrogenations.

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Biomasses, Drug Delivery and Hi-Tech formulative protocols: from Ca' Foscari University Lab to an innovative Start Up

E. Ghedini[a], F. Menegazzo[a], M. Signoretto[a]

[a] Ve Nice srl and CATMAT Lab, Department of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and INSTM-RU Venice, Via Torino 155, 30172 Venezia Mestre, Italy

Renewable resources, their use and transformation for pivotal industrial processes, have a key influence on our everyday life and are very interesting potentialities for an ever-growing cosmetic industry. The market for new, natural and bioactive ingredients in cosmetics is, in particular, very large and increasing. Many natural substances have bioactive effects such as preserving, healing, anti-inflammatory, antioxidant or emollient effects. Particularly appealing are ingredients derived from the biomass valorization, with attention to agri-food waste materials and from algal biomass. These biomasses are very rich in high value-added components, including essential oils, polyphenolic compounds, edible oils, pigments, dietary fibres, enzymes, etc.

Despite the immense potential, the transformation of biomass into bio-metabolites and their introduction in a cosmetic formulation implies a multidisciplinary and integrated approach. The first issue to face is the optimization of an efficient and sustainable protocol to extract the bio-actives from the biomass. Moreover, it must be considered that the use of biomass derived functional ingredients involves several critical issues concerning their complexity in term of molecular composition and physical features (color, granulometry, smell). These issues can be faced only by the exploitation of Hi-tech formulative protocols. Precisely with this spirit in 2018 it was born, from the heart of CATMAT (research team of SMN Department of Ca' Foscari University), Ve Nice srl: innovative Start Up and Spin Off of Ca' Foscari University. The core business of Ve Nice is represented by design of chemical specialties and formulation processes, in the cosmetic and nutra-cosmetic sectors in full accord with the paradigms of circular economy. The solid skills and expertise of Ve Nice, derived from years of research of CATMAT, have led to an Italian patent and an international patent applications [1]. The invention regards a sustainable and scalable process to produce a carrier made of components of natural origin or products derived from biomasses, for the formulation of high-tech cosmetic products with drug delivery features. The synergy between technology and biomasses valorization are a key point in all the Ve Nice products.

We briefly present the path which led to the foundation of Ve Nice: an effective example of technology transfer. We want to highlight our strengths but at the same time the issues encountered to face the market and to combine the researcher's vision with the entrepreneurial mentality.

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Assessment of the robustness of iron-based metal organic framework (MIL-88A) in aqueous environment.

Maryam Hmoudah[a,b], Vincenzo Russo[a,c], Martino Di Serio[a]

[a] *University of Naples Federico II, Department of Chemical Sciences, IT-80126 Naples, Italy.*
[b] *An-Najah National University, Department of Chemical Engineering, Nablus, Palestine.*
[c] *Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering, FI-20500 Turku/Åbo.*

Metal organic frameworks (MOFs) are a class of compounds that consists of metal ions and organic molecules that are linked together forming porous crystalline solid networks. Nowadays, these materials aroused massive attention among the scientific community due to the considerable promising applications in various fields such as gas adsorption and separation, CO_2 capturing, hydrogen and methane storage, water sorption, biomedical applications, etc.[1] Moreover, MOF hybrid structures development is drastically accelerating producing gigantic surface areas, different functionalities, and improved physical and chemical properties.[2] Nevertheless, these compounds showed high sensitivity when exposed to aqueous environment which may render the exploration of these compounds as effective heterogeneous catalysts.[3] Thus, further studies should be conducted in terms of design and optimized synthesis strategies of these materials to enhance their hydrolytic stability, cost, environmental impact, and sustainability towards potential industrial applications.[4] This work comprehensively investigates the robustness of MIL-88A experimentally. Stability experiments of these compounds were conducted in terms of chemical, thermal, hydrolytic, and mechanical rigidity. Different conditions as pH, temperature, soaking time in water and milling time, were controlled to meticulously understand the behavior of MIL-88A. The synthesis of this material was conducted in accordance with reported procedure under autogenous pressure.[5] Different characterization techniques were employed to study the crystallinity and the textural properties of MIL-88A such as XRD, SEM, TEM, BET, FTIR and UV-VIS DRS. Iron-based MIL-88A MOFs are designated as soft, porous crystalline materials and flexible MOFs. In other words, this class of MOFs can have structural transformations as crystal to crystal or crystal to relatively amorphous phase transitions as confirmed by the XRD patterns. Hence, understanding the unusual flexibility and the mechanism of these transitions of MIL-88A is assessed in this study. The detailed results of stability in terms of chemical, thermal, mechanical, and hydrolytic stability will be elaborated and showcased.

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Impact of gold nanoparticle stabilizing ligand in the selective oxidation of hydroxymethylfurfural over Au/C catalysts

Alessandro Allegri[a], Giulia Albanesi[a], Eleonora Monti[a], Stefano Scurti[a], Daniele Caretti[a], Nikolaos Dimitratos[a], Stefania Albonetti[a,b]

[a] Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy; [b] ISTEC-CNR, Institute of Science and Technology for Ceramics, National Research Council, Via Granarolo 64, Faenza, 48018, Italy.

Supported noble metal nanoparticles are a very important class of catalysts that can be applied in a vast number of processes. During their long history, the correlation between particle size and activity was made clear and extensively studied, revealing the necessity of stabilizing agents to prevent particle growth and aggregation.[1] Despite this, the effect of the stabilizing agent on the catalytic process is often overlooked, with attention being often paid only to particle size and interaction with the support. In this study, different polymers were employed as stabilizing agents for gold nanoparticles, and their effect was investigated applying the resulting catalysts in the selective oxidation of hydroxymethylfurfural (HMF), an important biomass-derived platform molecule, to 2,5-furandicarboxylic acid (FDCA), a prospective substitute of terephthalic acid for the production of biobased polyesters.[2]

An array of gold nanoparticles sols were synthesized using different commercial polymers as stabilizing agents and different Polymer:Au weight ratios. The polymers used were polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) and polyvinyl alcohol, while the Polymer:Au ratios were varied from 0.3 to 2.4. The gold nanoparticles were then characterized by means of DLS and ELS and immobilized on Activated Carbon (AC) via sol immobilization, yielding the final catalysts.[3] The Au/AC catalysts were characterized via TEM and tested in the selective oxidation of HMF. The results shown in Figure 1 highlight a different effectiveness of the different polymers in preventing the growth of the gold nanoparticles during their synthesis. More importantly, proof of a different behaviour of the stabilizing agents emerges from the varying correlation between particle size and FDCA yield when the polymer is changed.

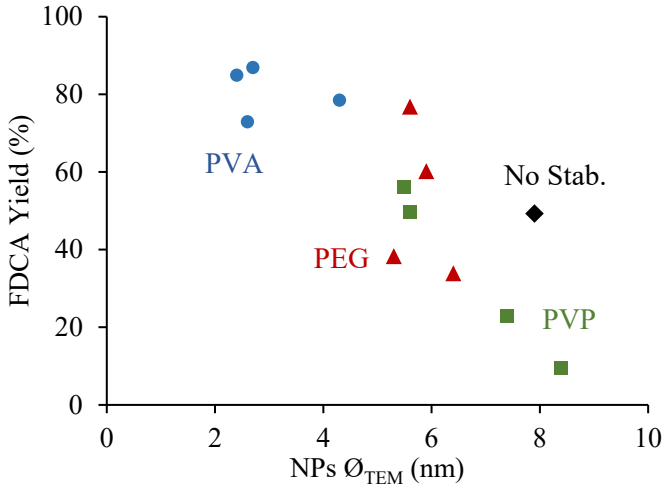

Figure 1. Effect of different stabilizing polymers on gold nanoparticles size and activity.

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The catalytic hydrogenation of 5-(hydroxymethyl)furfural: a comparison between batch and continuous flow approaches

Giulia Balestra[a] , S. Solmi[a] , A. Sacchetti[a], T. Tabanelli[a], F. Cavani[a]

[a] Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale del Risorgimento, 4, 40136 Bologna (Italy)

The production of biomass-derived fuels and chemicals is of great importance for the transition to a more sustainable future. In this context, 5-(hydroxymethyl)furfural (HMF) has been identified as a key precursor for the production of biofuels and high added value chemicals. Moreover, the products obtained by hydrogenation of HMF are potential sustainable substitutes for petroleum-based building blocks used in the production of chemicals.[1,2] Among them, 2,5-bis(hydroxymethyl)furan (BHMF) is widely used as an intermediate for the synthesis of resins, fibers, foams, drugs, polymers and crown ethers; its further reduction to the formation of 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF), which can be used as green solvent and monomer.[2] Additionally, the hydrogenolysis of HMF generates 2,5-dimethylfuran (DMF), and from its consecutive hydrogenation it is possible to obtain 2,5-dimethyltetrahydrofuran, both are promising bio-fuel additives.[1] In this work, the catalytic hydrogenation of HMF has been investigated over three supported Pd heterogeneous catalysts. Two of them were made of palladium supported on carbon with different metal loadings, 1 and 10 wt%, both being commercial samples. The catalyst consisting of palladium supported on γ-alumina, 1 wt% Pd/γ-Al_2O_3, was prepared in the lab through the so-called "sol-immobilization" method.[3] The reactions were performed in liquid phase working in both batch (stainless steel autoclave) and continuous-flow (H-Cube Mini, developed by ThalesNano Inc.) reactors and water (or bio alcohols) was selected as benign solvent. In this way, the effects of the main reaction parameters, such as temperature, hydrogen pressure and reaction time/contact time have been investigated in detail. By working at 90°C and 50 bar of hydrogen over the Pd/C 10 wt% catalysts and choosing the optimal contact time in the flow reactor system, the selectivity of BHMF achieved was up to 76% with complete HMF conversion. With the batch system, the production of secondary products was favored as well as lowers value of carbon balance, proving the importance of the reaction set-up in enhancing the selectivity toward an intermediate product such as BHMF. Some by-products (named "others" in Figure 1) given by the subsequent hydrogenolysis, hydrogenation and ring opening reactions of the main products were identified in the reaction mixture by GC-MS. According to the results obtained, a reaction pathway that needs future investigation has been proposed (Figure 1).

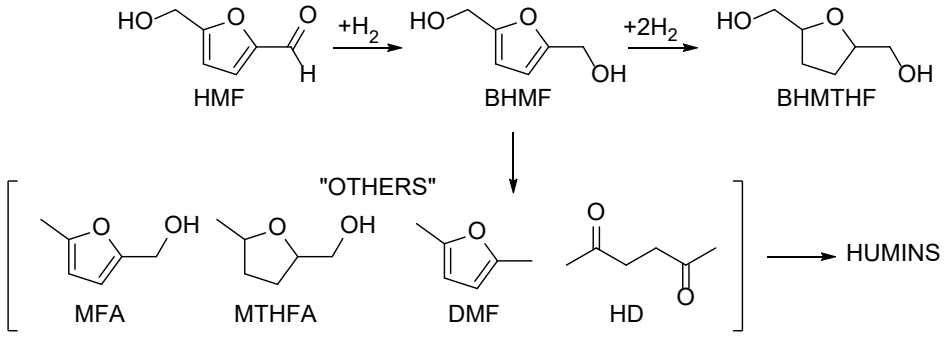

Figure 1. Reaction network proposed for the hydrogenation and hydrogenolysis of HMF in water. (MFA: 5-methylfurfuryl alcohol; MTHFA: 5-methyltetrahydrofurfuryl alcohol; DMF: 2,5-dimethylfuran; HD: 2,5-hexanedione)

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Pyrolysis of lignocellulosic materials

Massimo Bernardini,[a] Gustavo Capannelli,[a] Camilla Costa,[a] Reshma Babu,[a] Antonio Comite,[a]

[a] Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, via Dodecaneso, 31, 16146 Genova

Introduction

Lignocellulosic biomass is a renewable energy source widely available. Traditionally, the main process used to produce energy from lignocellulosic materials has been combustion. However, this process is losing interest due to high carbon dioxide (CO_2) and ashes emissions. Recently, thermochemical technologies have been studied, thanks to the possibility to obtain liquid fuels, also known as bio-oils, and other organic compounds and gaseous products which can be exploitable in the pursuit of a more circular economy.

The main components of lignocellulosic materials are cellulose, hemicellulose and lignin. The products obtainable from the pyrolysis process using these biomasses as feed depend on the nature of the material and on the type of reactor and operative conditions, such as temperature and heating rate. Hemicellulose is the most thermolabile component, showing degradation under 300 °C. The main products are char and gas. Cellulose degrades at slightly higher temperature, near 350 °C, and from this feed high yields of bio-oil and gas are produced. The degradation of lignin starts at lower temperature than cellulose, however, it takes place in a wider temperature range, until 700 °C. At 500 °C the main products are char and gas, but it is possible to obtain bio-oil at higher temperature. In this work, preliminary results of pyrolysis of lignocellulosic materials will be showed.

Experimental

The process was conducted in a lab-scale plant using cellulose, lignin, cellulose-lignin mixture (25%-75%, 50%-50%, 75%-25%), and waste wood, as an example of a real lignocellulosic material, as feed. Firstly, every material was characterized using thermogravimetric analysis (TGA) to identify the proper temperature of the process. Then, pyrolysis processes were carried out at different temperatures between 350 and 500 °C in a vertical quartz reactor, using a nitrogen atmosphere. During the process, production of gas was monitored using gas chromatography, and yields of char, liquid and gaseous products was calculated. Some liquid products were identified using Fourier transform infrared spectroscopy (FTIR) and gas chromatography-mass spectroscopy (GC-MS).

Results

Pyrolysis of cellulose showed lower char yield and higher liquid yield increasing the temperature of the process. The main gas obtained were carbon dioxide and carbon monoxide (CO), while the yields of methane (CH_4) and hydrogen (H_2) were lower. Higher yields of gaseous products were obtained increasing the temperature from 350 to 400 °C.

Pyrolysis of lignin has not produced liquids with the operative conditions adopted, while yields of CH_4 and H_2 were higher than cellulose. Pyrolysis of cellulose-lignin mixtures showed unexpectedly high liquid yields. Furthermore, GC-MS analysis showed the formation of molecules which were not obtained from the pyrolysis of cellulose and lignin carried out separately.

Lastly, pyrolysis of waste wood was performed, showing results comparable to those obtained from the cellulose-lignin mixture 75%-25%.

New innovative materials from saccharide sources

Alice Cappitti[a], Silvia Giorgi[a], Roberto Giannelli[a], Antonella Salvini[a]

[a]Department of Chemistry "Ugo Schiff" University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (Italy)

The interest of academia and industry for the use of renewable resources as starting material has assumed a central role in the modern chemical industry. In particular, in the biorefinery processes, the saccharides obtainable from lignocellulosic biomasses play an important role in accordance with the requirements of low environmental impact and taking also into account the principles of the Green Chemistry.
In this work, new biopolymers were synthesized using α,α'-trehalose as feedstock to obtain monomers with a structure containing polar and reactive groups capable of influencing the application behavior of their polymeric derivatives.
The α,α'-trehalose is a non-reducing disaccharide derived from the condensation of two glucose molecules, with high chemical stability which can be used as an interesting substrate in the synthesis of biocompatible and biodegradable monomers, due to its wide presence in nature. In fact, this saccharide can be found in many organism (bacteria, fungi, insects, plant and invertebrates) or more interestingly can be obtained from starch to a relatively low cost using enzymatic methods.
In this research, two different synthetic procedures were used to functionalize α,α'-trehalose in order to obtain monomers for the following polymerization.
The first saccharide monomer was synthesized using allyl bromide to functionalize trehalose, obtaining products whose degree of functionalization varies according to the molar ratio between the reagents [1]. These bio-based monomers were subsequently used for the synthesis of vinyl acetate copolymers through radical copolymerization reaction and three different molar ratios between the two monomer units were selected to evaluate the influence of the composition on the chemical properties.
Then, the second methodology involved the synthesis of acrylic derivatives through a transesterification reaction using ethyl methacrylate to functionalize trehalose. In this case, the monomers were used for the synthesis both vinyl acetate copolymers and ethyl methacrylate copolymers, always through radical copolymerization reaction. All these copolymers were synthesized with different molar ratio between the two monomer units in order to evaluate the role of composition on the different chemical properties of the copolymers.
All the monomers and the copolymers were characterized using FT-IR and NMR spectroscopies and studies were carried out to evaluate the behavior in terms of solubility of the products.

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A MALDI-TOF Based Procedure to Determine the Compositions of Polymer Brushes Obtained by Grafting To Reactions of Hydroxy-Terminated Polystyrene Samples

Riccardo Chiarcos[a], *Diego Antonioli*[a], *Valentina Gianotti*[a], *Michele Perego*[b], *Michele Laus*[a]

[a]*Department of Science and Technological Innovation, University of Piemonte Orientale, viale T. Michel 11, 15121, Alessandria Italy.*
[b]*Laboratorio MDM, IMM-CNR, Via C. Olivetti 2, 20864 Agrate Brianza, MB, Italy*

In the last fifty years, polymer brushes have gained a central role as surface modifiers and are actually employed in several different applications, from nanolithography to antifouling systems. Generally, polymer brushes are obtained by reacting some functional polymers with the substrate in a process named "grafting to reaction". Because approximately all the synthetic polymers are characterized by broad mass distributions, a preferential reactivity of the shortest (longest) chains during the grafting to reaction could strongly reduce (increase) the average molecular weight of the final brush. Although the knowledge of the real average molecular weight of the grafted polymers is essential because it strongly defines the mechanical and functional properties of the brush, the reduced amount of material makes the information difficult to access experimentally.
In this work we have developed an analytical method based on MALDI-TOF analysis to accurately measure the composition of brushes obtained by grafting a mixture of polystyrene samples with different molecular weights. Primarily, different mixtures with known compositions were used to calibrate the instrument. Then, considering that the grafting to reaction was conducted starting from a spin-coated layer of the polymer mixture, the chains that are not reacted with the surface after the grafting process were collected and analyzed. Finally, knowing the composition of both the starting mixture and the unreacted part of the spin-coated layer, the brush composition was evaluated by difference.
The method was finally validated and employed demonstrating a significant brush enrichment of short chains during the grafting to reaction.

Kinetic of peroxyformic acid decomposition

Tommaso Cogliano, Rosa Turco, Vincenzo Russo, Martino Di Serio & Riccardo Tesser*

Department of Chemical Science, University of Naples "Federico II", Complesso Monte Sant'Angelo, 80126, Naples, Italy

Percarboxylic acids, also called peracids, have gained interest in many chemical fields during the last decades. Industrially their finds application mainly in paper-pulp bleaching, as disinfectants for drinking water, oxidation of aqueous pollutants, sludge treatment, in the epoxidation of unsaturated hydrocarbons and the esterification of ketones, to name just a few examples. Peracetic acid (PAA) and performic acid (PFA) are industrially the most relevant peracids since they have the highest oxidation potential [1]. Both are thermodynamically unstable and can decompose spontaneously or explode when they are highly concentrated. However, performic acid has shown to be more active than peracetic acid, making it a more popular oxidizing agent despite its easier decomposition also at room temperature [2]. They are simply prepared by putting the corresponding carboxylic acid in contact with a solution of hydrogen peroxide either in presence of an acid catalyst or in auto-catalyzed mode. The formation is more or less a quick equilibrium reaction meanwhile the decomposition reaction is an irreversible reaction that could happen following several pathways, namely radical or ionic. Nevertheless, there are only a few articles available in the literature concerning percarboxylic acids formation and there is a lack of information about the decomposition reaction [2-4]. Moreover, the available papers were mainly focused on the peracetic acid formation than peroxyformic acid. Thus, the peroxyformic acid reactions kinetics were studied mainly focusing on the decomposition reaction through the measurement of the evolved gas over time. Several runs were carried out, firstly hydrogen peroxide degradation was checked adopting the same conditions set up in the peroxyformic reaction, then the reaction was evaluated in presence of a mineral acid (H_3PO_4) and in autocatalytic mode changing temperature, reactant molar ratio and reaction time to allow a rigorous kinetic study. Finally, a kinetic model was developed to interpret all the kinetic runs performed and determining the kinetic parameters with the best fits.

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Efficiency comparison of advanced oxidation processes (AOPs) for the mineralization of azo-dyes in water

F. Conte[a], C. Calloni[a], A. Tripodi[a], G. Ramis[b] and I. Rossetti[a]

[a] *Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano, CNR-ISTM and INSTM Unit Milano-Università, via C. Golgi 19, 20133 Milan, Italy;*
[b] *Dip. Ing. Chimica, Civile ed Ambientale, Università degli Studi di Genova and INSTM Unit Genova, via all'Opera Pia 15A, 16145 Genoa, Italy*

The aim of this work was to find out a sustainable and scalable process in order to treat dye-rich wastewaters from textile industries and fully degrade these organic pollutants to non-harmful substances. Different chemical, photochemical and photocatalytic processes have been compared to find the most suitable for this application, either in terms of technical feasibility and with a look to the safety of the treated wastewaters.
The Dystar's Levafix Brilliant Red E-6BA dye was used as a model molecule and treated through different advanced oxidation processes (APOs): H_2O_2/UV, Fenton and Photo-Fenton reactions, defined as homogeneous phase reactions, to be further compared with heterogeneous photocatalyzed processes. The use of heterogeneous titania may be advantageous since the catalyst can be separated and re-used after the treatment, in contrast with the iron salt used for Fenton reaction which forms sludges. Moreover, metallic co-catalysts can be deposed over TiO_2 nanoparticles in order to tune the light harvesting properties and activity.
The various reaction parameters, such as pH, concentration of oxidant, quantity of Fe catalyst, type of light source (dark, LED, sunlight and UV) were changed and optimized to shorten the degradation time.
The best results were observed when using a low-power UV lamp directly immersed into the solution, as the time required to degrade 100 ppm solution of dye (pH 7, 25 °C, 36 mg/L of catalyst, 1 equivalent of oxidant) was ca. 10 minutes for both Photo-Fenton and UV/H_2O_2 processes, compared with 160 minutes required to complete the degradation in dark conditions. The reaction time almost doubled (20 min) when employing an external UV lamp, while both visible LED and solar light sources were comparable in terms of results (ca. 50 min), but the latter strictly depended on the weather conditions.
The treatment with 50 ppm of titania P25 was very effective when using an UV lamp directly immersed into the solution (irradiance = 260 W/m^2), indeed more than 95% of the pollutant was degraded in ca. 40 min and we observed even better performance when adding hydrogen peroxide to the reactor (4 eq. H_2O_2, 8 min).
To conclude the feasibility assessment, the 48-LC_{50} values of the treated samples were determined performing the acute toxicity test using *Daphnia magna* to check the toxicity of the final products. The treated solutions were characterized by acute toxicity, even higher than the original dye when H_2O_2 was used. Since COD tests revealed that for most cases there was no residual organic carbon into the treated solution, the noxious effects were mainly attributed to the residues of hydrogen peroxide. This poses severe limits for the application of these technologies, at difference with heterogeneous photocatalytic processes, which may be slower, but by far safer, even when using nanostructured TiO_2, which revealed no acute toxicity effect for the selected organisms.

Investigating the crosslinking system role in the force production of Liquid Crystalline Networks

S. Donato,[a,b] D. Martella,[a,b] D. S. Wiersma,[a,b,c] C. Parmeggiani[a,b,d]

[a] *European Laboratory for Non-linear Spectroscopy, via Nello Carrara 1, Sesto Fiorentino (FI)*
[b] *Department of Physics and Astronomy, University of Florence, Via Sansone 1, Sesto Fiorentino (FI)*
[c] *Istituto Nazionale di Ricerca Metrologica (INRiM), Strada delle Cacce 91, Torino*
[d] *Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, Sesto Fiorentino (FI)*
donato@lens.unifi.it

Liquid Crystalline Elastomers (LCEs) are among the best candidates, within smart materials, for cardiac tissue engineering, given their ability to act in response to an external stimulus (light, temperature, etc.).[1] Our state-of-the-art material can achieve a force development of 70 mN/mm^2 at a power of 1.5 W/mm^2, through a combined thermal/optical process. Our current goal deals the design and synthesis of new molecules to improve of the material force development by decreasing the energy supplied.[2] Therefore, we are working on the realization of a new cross-linker palette possessing bulky substituents (tert-butyl, trimethyl and dimethyl) in the aromatic cores. Introducing different substituents, it will be possible to decrease the interactions among a LC molecule and its nearest neighbors. Ideally, this should lead to a subsidence of the nematic-to-isotropic phase transition temperature, and thus a reduction in the amount of energy needed to obtain the force development of the material. Here we present the new pathway of reaction developed to obtain such bulky liquid crystals cross-linkers. The obtained molecules were used to prepare smart materials which liquid-crystal, thermal, optical, and mechanical properties were deeply analyzed. The improved materials will be further presented for *in vitro* application.

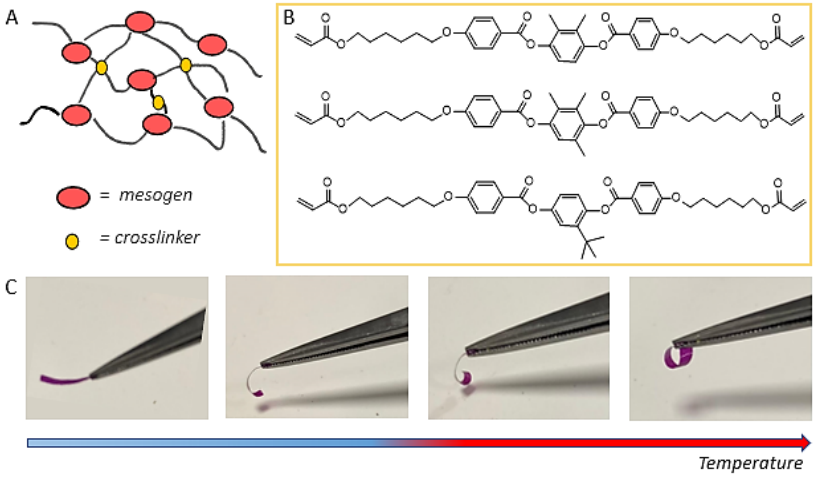

Figure 1: A) General structure of a liquid crystal mixture, B) Different structures of the new crosslinkers, C) actuation of the material under temperature.

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Effects of SiO_2-based scaffolds in TiO_2 photocatalyzed CO_2 reduction

Giulia Forghieri[a], Danny Zanardo[a], Elena Ghedini[a], Federica Menegazzo[a], Alessandro Di Michele[b], Giuseppe Cruciani[c], Michela Signoretto[a,]*

[a] *CATMAT Lab, Department of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and INSTM-RU Venice, Via Torino 155, 30172 Venezia Mestre, Italy*
[b] *Department of Physics and Geology, University of Perugia, Via Pascoli, 06123 Perugia, Italy*
[c] *Department of Physics and Earth Science, University of Ferrara, Via Saragat 1, 44122 Ferrara, Italy*

The process of CO_2 photo-reduction has emerged as appealing opportunity to upgrade a waste gas into valuable fuels or chemicals, due to mild reaction conditions and the possibility to use sunlight as energy source [1]. Amongst the several semiconductors (SC) materials considered, titanium dioxide (TiO_2) is one of the most popular material used as catalyst for this reaction, being abundant, cheap, photo-stable and non-toxic, but also having poor activity [2]. In general, the main limiting features to TiO_2 application consist in fast charge carrier recombination and its wide band gap (3-3.3 eV), resulting in effective photo-activity only in the UV region [3]. The proposed strategies to overcome these issues are surface modification with a co-catalyst, visible-light sensitizing and scaffolding of the active phase. The use of transparent and porous materials has been proposed to favour reagent adsorption [4, 5], and only recently to promote light scattering as mean to increase photo-activity of the dispersed catalyst [6]. Mesoporous silica (SiO_2), such as SBA-15, used as scaffolding material led to increased activity compared to TiO_2 nanoparticles (NPs) however leading to H_2 generation [7]. The latter is generally considered a side product reaction, competing with the generation of the main product (CH_4) from H_2O.

While the effectiveness of mesoporous scaffolds in improving CO_2 photo-conversion has already gained attention, no macroporous materials have yet been successfully applied or reported, to the best of our knowledge. In this study, we report a comparison of the effect of macro- and mesoporous silica on the photocatalytic performance of TiO_2 over CO_2 photo-reduction. A benchmark TiO_2 was supported on a macroporous SiO_2 and mesoporous SBA-15. The materials were both tested for CO_2 photo-reduction and as CO_2 capture-and-conversion hybrid systems.

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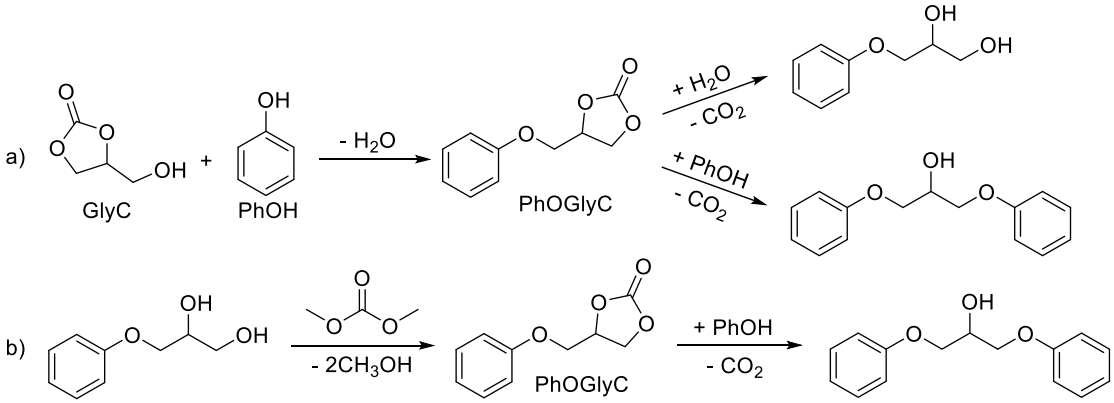
Glycerol carbonate as innovative alkylating agent in phenyl-glyceryl ethers synthesis

G. Galletti,[a] *S. Vanzini*,[a] *R. Mazzoni*,[a] *R. Cucciniello*,[b] *F. Cavani*[a] *and T. Tabanelli*[a]

[a] *Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale del Risorgimento 4, I-40136 Bologna, Italy.* [b] *Dipartimento di Chimica e Biologia "Adolfo Zambelli", University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy.*

In the last decades, organic carbonates (OCs) have gathered growing interest and importance in chemical processes, being potentially synthesizable directly from carbon dioxide and alcohols and displaying good biodegradability and low toxicity. [1] In this context, glycerol carbonate (GlyC) represents an interesting example, bearing both a cyclic carbonate moiety and a free hydroxyl group, which confer peculiar properties and a versatile reactivity. Moreover, it finds applications as a solvent, as an electrolyte carrier in batteries, as intermediate in pharmaceutical preparations and in many other fields. [2] Noteworthy, our group has recently proved the peculiar role of GlyC as innovative alkylating agent for catechol to obtain 2-hydroxymethyl-1,4-benzodioxane (HMB), an important intermediate in the synthesis of pharmaceuticals. The reaction is highly selective and efficient in the presence of cheap basic catalysts and has been patented. [3] Encouraged by these results, GlyC has been tested in the alkylation of phenol (PhOH) to obtain both mono and di-phenyl glyceryl ethers (PGEs), interesting intermediates for the synthesis of pharmaceuticals and surfactants, through a reaction scarcely investigated in literature. [4] A wide plethora of both homogeneous and heterogeneous basic catalysts (e.g. $NaOCH_3$, MgO and Na-mordenite) has been considered and the effect of different reaction parameters (e.g. temperature, reagent molar ratio) has been investigated. Interestingly, after only one hour of reaction between phenol and a slight excess of GlyC at 170 °C (6,6 mol% K_2CO_3) it was possible to obtain a full conversion of both the reagents and good yields in monophenoxy glycerol (3-phenoxy-1,2-propanediol) and diphenoxy glycerol (1,3-diphenoxy-2-propanol), respectively 54% and 24%. Moreover, a multi-step approach for the selective production of diphenyl glyceryl ethers has been investigated by reacting the mono-PGE with dimethyl carbonate to obtain the intermediate 4-(phenoxy)methyl-1,3-dioxolane-2-one (phenoxy glycerol carbonate, PhOGlyC), which was reacted with phenol to obtain the diphenoxy glyceryl ether (Scheme 1).



Scheme 1: a) reaction between GlyC and phenol to yield mono- and diphenylglyceryl ethers; b) multi-step approach for the selective synthesis of diphenylglyceryl ether.

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Photocatalytic reforming of Glycerol for hydrogen and chemicals production.

Valeriia Maslova[a], Pio Gramazio[a], Andrea Fasolini[a], Stefania Albonetti[a], Francesco Basile[a].

[a] Department of Industrial Chemistry "Toso Montanari", Alma Mater Studiorum – University of Bologna, Viale del Risorgimento, 4, 40136 Bologna, Italy

In recent years there have been intensive efforts toward the development of novel technologies for the production of hydrogen from renewable resources, mainly water and biomass[1]. Among the feasible compounds proposed as substrate for hydrogen production, glycerol ($C_3H_8O_3$) is of special interest because it is produced in large amounts (10 wt.%) as by-product of transesterification for biodiesel production[2]. Hydrogen can be produced at ambient condition via an efficient, technologically-simple, ecologically-benign and potentially low-cost process with the use of TiO_2 and solar light[3] in the photo-reforming reaction. In the present work the effect of the TiO_2 semiconductor synthetic pathway and noble metal co-catalyst addition were investigated on photo-reforming of glycerol under base-free, ambient, anaerobic conditions. Commercial TiO_2 powders, Cristal ACTiV DT-51 and Degussa P25, were confronted with lab-made TiO_2 obtained via inverse microemulsion method[3,4]. The semiconductor was fully characterized by XRD, nitrogen physisorption, TEM and UV-vis reflectance analyses. Reverse microemulsion-based synthesis allowed to prepare of nanosized TiO_2 particles of anatase or rutile crystalline phases depending on the reaction conditions. The resulted nano-oxides were found to have smaller average crystalline size, higher surface area and narrower band gap than commercial TiO_2 samples, P25 and DT-51. Lab-made TiO_2 rutile revealed higher H_2 production when bare supports were compared. The TiO_2 materials were, also, used as supports for platinum nanoparticles prepared by incipient wetness impregnation and deposition-precipitation methods. Among the metal-decorated catalysts tested, Pt nanoparticles prepared by deposition-precipitation showed the most promising results towards hydrogen production, because of the small and homogeneously distributed nanoparticles compared to classical impregnation method. Rutile obtained higher results when impregnated because Pt dispersion resulted more homogeneous and of smaller dimension. Nevertheless, P25-based materials outperformed the other types of titania supports in hydrogen production. Further comparison of the results demonstrated that P25, lab-made anatase and rutile based catalysts exhibited higher production rates of glycolaldehyde, while DT-51 based ones showed slightly greater productivity to glyceraldehyde than glycolaldehyde. Also, comparison between lab-made metal decorated TiO_2 materials showed higher production rates with Rutile phase.

However, the difference in apparent density between the synthetized and commercial titania samples, which may affect light absorbance during the reaction, made a complete comparison of the catalytic performances difficult. Thus, further synthesis optimization led to production of microemulsion synthetized powders with lower density together with the peculiar morphological and catalytic properties provided by this synthetic method. Low density samples, when tested, showed promising results, with higher H_2 production rate than standard microemulsion synthetized TiO_2 and commercial P25.

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The role of Liquid Crystalline Elastomers towards the Development of Active Cell Culture Substrates

B. Grandinetti[a,b], M. Rojas[a], D. Liu[c], D. Martella[a,f,h], S. Querceto[d,e], C. Ferrantini[e], J. M. Pioner[e], C. Tesi[e], D. J. Broer[c], D. S. Wiersma[a,b,h], C. Poggesi[a,e], L. Sacconi[a,g], C. Parmeggiani[a,f]

[a] European Laboratory for Non Linear Spectroscopy, Università degli Studi di Firenze, Sesto Fiorentino (Italy); [b] Department of Physics and Astronomy, Università degli Studi di Firenze, Sesto Fiorentino (Italy); [c] Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven (The Netherlands); [d] Department of Molecular and Developmental Medicine, Università degli Studi di Siena, Istituti Biologici S. Miniato, Siena (Italy); [e] Department of Experimental and Clinical Medicine, Università degli Studi di Firenze, Firenze (Italy); [f] Department of Chemistry "Ugo Schiff", Università degli Studi di Firenze, Sesto Fiorentino, (Italy); [g] National Institute of Optics, National Research Council, Sesto Fiorentino (Italy); [h] Istituto Nazionale di Ricerca Metrologica (INRiM), Torino (Italy);

Liquid Crystalline Elastomers (LCEs) have proven to be good candidates for the next generation of biomedical implants and devices, thanks to their stimulability, tunable response time and biocompatibility. In these materials, the molecular reorganization induced by stimulation drives a macroscopic shape change [1–3]. Liquid crystallinity enables intrinsic thermal and electric/magnetic-field-responsiveness, while mechanical properties are easily changed by tuning the crosslinking density of the polymer network; light stimulation is enabled via the addition of a dye to the composition of the monomer mixture. [4]

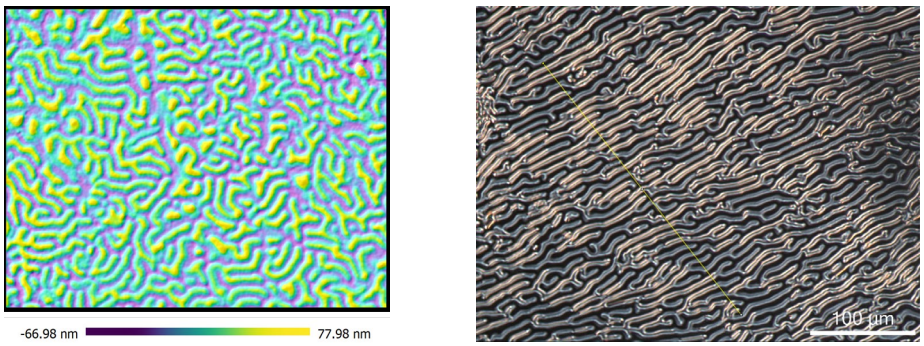

Figure 1: An example of fingerprint-patterned surface, obtained by self-assembly of chiral nematic LCEs on a homeotropically-aligning surface. Left: surface topography in the unactuated state; right: polarized optical microscope image of the fingerprint coating.

LCEs are also one of the few examples of cell-instructive materials: the anisotropy of their network has been shown to enhance cell alignment, which positively affects cell functionality in different lines. [5] In this contribution, the latest advances of the use of LCE-based materials in the field of Regenerative Medicine and Tissue Engineering will be reviewed. The communication will focus on the effect of responsive fingerprint-patterned surfaces, originated by self-assembly of chiral nematic LC molecules, on cell growth and functionality (Figure 1). [6] New fabrication and processing techniques, such as 3D printing, will also be discussed. [7] The research leading to these results has received funding from Ente Cassa di Risparmio di Firenze, grant n. 2020/1583.

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Nonconventional Technologies and Natural Deep Eutectic Solvents: Synergistic Application for Bioactives Recovery from Blueberry-Peels

Giorgio Grillo,[a] *Veronika Gunjević*,[a,b] *Kristina Radošević*,[b] *Ivana Radojčić Redovniković*, [b] *Giancarlo Cravotto*[a]

[a] *Department of Drug Science and Technology, University of Turin, Via P. Giuria 9, 10235 Turin, Italy;*
[b] *Department of Biochemical Engineering, Laboratory for Cell Culture Technology and Biotransformations, Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottojeva ulica 6, 10000 Zagreb, Croatia.*

Waste reduction *via* reuse and recycling is one of the main principles of the circular economy [1], preferable to actual prevailing waste management methods. The food industry produces large amounts of waste and byproducts, source of environmental pollution due to high chemical- and biological-oxygen demand. Concurrently, the disposed biomasses possess significant concentration of valuable metabolites. In recent years consume of blueberries has increased thanks to their bioactivity and health promoting effects. In particular, they possess a dramatic antioxidant activity, mainly due to their exceptional concentration of anthocyanins [2]. The highest content of these polyphenols can be found in the external part of the fruit and it is worth noting that blueberry peels (BP) are one of the main residues in blueberry fruit processing. The beneficial health effects of dietary anthocyanins have been recognized in literature according to epidemiological and clinical researches. Their strong antioxidant activity results into positive effects on the prevention of cardiovascular disease, while they also show antiproliferative, anti-inflammatory, and neuroprotective activity [3]. Highly efficient solid–liquid extraction facilitates the convenient recovery of high-value secondary metabolites from food byproducts. Extraction is the crucial unit operation and, can lead to high energy consumption, as well as low extraction yield and selectivity.
Interest in bioactive phytochemicals and sustainable processes is the driving force behind this study on two novel green extraction methods, aiming to recover anthocyanins from BP [4]. Five natural deep eutectic solvents (NaDES) have been tested for extractions, adopting acidified hydroalcoholic solutions as benchmark. Shelf life of eutectic systems was monitored as well. The most promising NaDES was tested for microwave (MAE)- and ultrasound-assisted extractions (UAE), describing the related kinetics. MAE and UAE yielded up to 25.83 and 21.18 mg/g_{matrix} of total anthocyanin content respectively (after 15 and 30 min). Both technologies provided performances superior to conventional reference. Finally, the antiproliferative activity of the products was determined by a Cell Proliferation Assay, the so-called MTS assay, on human tumor HeLa (human cervical adenocarcinoma) cells and human skin HaCaT (normal human keratinocyte) cells. Nonconventional extracts exhibited strong antiproliferative activity that was much greater than that of their conventionally extracted analogues. Flow cytometry, exploited to determine cell-death type, pointed out apoptosis as the primary cause of tumor cell death. The presented study demonstrated the synergistic effects of enabling technologies together with green solvents application. Hence, an antiproliferative agent can be recovered from a food industry residual biomass.

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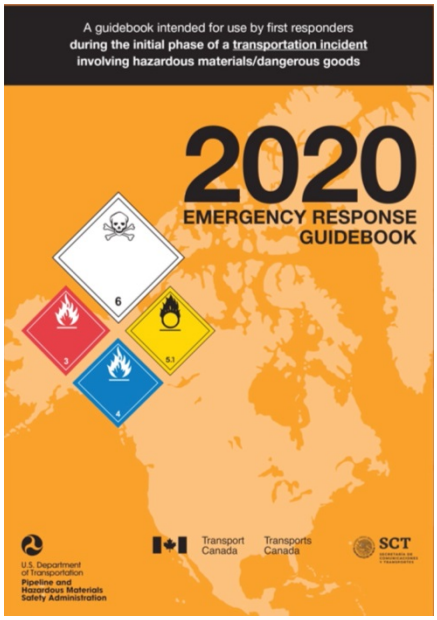
Enhancing capabilities for the mitigation of chemical risk: the dissemination of the Emergency Response Guidebook (ERG) in Italy

Matteo Guidotti[a], Luca Prodi[a], Aldo Roda[a], Claudio Trombini[a], Daniele Meuti[b], Mario Matteucci[b], Gaetano Carminati[b]

[a] Accademia delle Scienze dell'Istituto di Bologna, via Zamboni 31, Bologna; [b] Autorità Nazionale per l'attuazione della Convenzione sulla Proibizione delle Armi Chimiche, MAECI, p.le Farnesina 1, Roma



The Emergency Response Guidebook (ERG) is an extremely useful reference manual used by many first responders worldwide [1]. The guidebook was developed by Transport Canada, the US Department of Transportation and the Secretariat of Transport and Communications of Mexico. It assists rescue professionals in recognizing accidents involving hazardous chemicals, identifying life-threatening substances, selecting protection and evacuation strategies, mitigating damages on victims and the environment and, ultimately, saving lives.
The ERG is published every four years in English, French and Spanish. No Italian version of the text has been published so far and this limits the use of it by some professionals in Italy.

A wider knowledge of this manual will broaden the range of final users and will enhance the preparedness and response capability both in the private and public sector. This will address public safety concerns, environmental protection and resilience against unintentional natural events, industrial accidents or criminal acts involving the use of hazardous chemicals.

The work of the chemical section of the Academy of Science of the Institute of Bologna [2] aims at promoting the circulation of the ERG manual across non-specialist professionals and first response operators in Italy. A parallel awareness-raising campaign, with seminars and tutorial sessions about its correct use will be promoted by the members of the Academy of Bologna not only in schools and high education institutions, but also in public and private sectors involved in the prevention and mitigation of risks related to unsafe or incorrect uses of Chemistry.
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Such an initiative is supported by the Department of Chemical Sciences and Materials Technologies of the Italian Research Council (CNR) [3] with the cooperation of Italian National Authority for the Implementation of the Convention on the Prohibition of Chemical Weapons (CWC) [4].

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Nickel based catalysts for Methane DRY Reforming: two synthetic procedures are compared

Valeria La Parola[a], Maria Luisa Testa[a], Leonarda Francesca Liotta[a], Giuseppe Pantaleo[a], Tatyana Tabakova[b], Anna Maria Venezia[a]

[a] *Istituto per lo Studio dei Materiali Nanostrutturati (ISMN), Consiglio Nazionale delle Ricerche (CNR), Via Ugo La Malfa 153, 90146 Palermo, Italy;* [b] *Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Bl. 11, 1113 Sofia, Bulgaria*

Strong correlation between global warming with consequent climate changes and the increase of CO_2 being emitted into the atmosphere by human activities has been ascertained. Finding solution to diminish the CO_2 is one of the main issues in environmental research. Among various approaches being proposed, dry reforming of methane (DRM) consisting in the reaction of CO_2 with CH_4 to produce syngas ($CO + H_2$) is a promising procedure. The process requires catalysts with high activity and long-term stability. In this work we investigate the DRM catalytic activity of Ni based catalysts. Two series of catalysts supported on Ti or Zr doped silica, with molar ratio Ti/Si =Zr/Si =0.1, obtained by means of two synthetic sol gel procedures, one pot (**sg-op**) and grafting (**sg-gr**), are compared.
The SiO_2-TiO_2 and SiO_2-ZrO_2 mixed oxides were prepare The **sg-op** supports were prepared by one pot acidic hydrolysis of the respective alkoxides (with acetic acid at pH 5). The **sg-gr** supports were prepared by refluxing a toluene solution containing the Ti or Zr propoxides on solgel prepared silica surface. The obtained oxides were dried overnight at 110 °C and calcined at 450 °C for 4h. Thereafter nickel was introduced by dry impregnation using nickel nitrate as precursor. The catalysts with 10 wt% Ni loading were calcined at 650 °C for 4h. The samples were analyzed by X-Ray diffraction, X-Ray photoelectron Spectroscopy, H_2 Temperature Programmed Reduction, N_2 Physisorption and Thermogravimetric Analysis.
The two support preparation procedures yield samples with similar surface area (between 250 and 350 m^2g^{-1}) but very different structures as evidenced by X Ray Diffraction patterns showed in Figure 1. The **sg-op** samples exhibit large Ni particles without segregated titania or zirconia, while the **sg-gr** display smaller Ni particles and crystallized ZrO_2 or TiO_2.

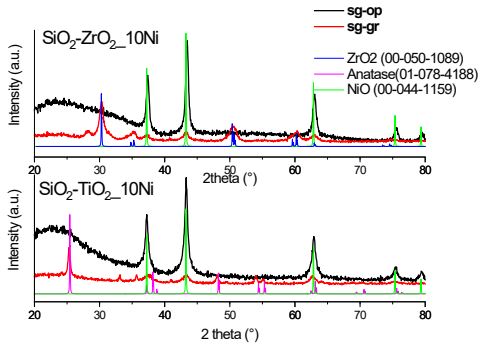

Figura 1 XRD of calcined catalysts

The DRM catalytic activity was tested in a continuous flow reactor with a feed mixture of 15 % CH_4, 15 % CO_2 and 70 % He at GHSV of 60000 $mLg^{-1}h^{-1}$and at 650 °C. The correlation between the structure and the DRM activity is here analyzed.

Acknowledgement
The bilateral project between CNR and Bulgarian Academy of Science (BAS) is kindly acknowledged

Photoelectrocatalytic remediation system for ammonia in water

Simone Livolsi[a], Gian Luca Chiarello[a], Annamaria Costa[c], Alessia Di Giancamillo[b], Chiara Bazzocchi[b], Eleonora Buoio[c], Massimiliano Bestetti[d], Silvia Franz[d], Elena Selli[a]

[a]Dep. of Chemistry, University of Milan, Via Golgi 19, 20133 Milano, Italy; [b]Dep. of Veterinary Medicine, University of Milan, Via dell'Università 6, 26900 Lodi; [d]Dep. of Health, Animal Science and Food Safety (VESPA) University of Milan, Via dell'Università 6, 26900 Lodi; [c]Dep. of Chemistry, Materials and Chemical Engineering "Giulio Natta", Polytechnic of Milan, Piazza Leonardo da Vinci 32, 20133 Milano

Ammonia, produced by human and animal activities, contributes to water and soil pollution because it is toxic for aquatic both flora and fauna, and responsible for eutrophication [1]. In this work, the photoelectrocatalytic (PEC) oxidation of ammonia is investigated as an alternative or complementary remediation process to the traditional biological ones [2]. For this purpose, a stainless-steel PEC reactor was employed, consisting of a central UVA Hg-vapor lamp surrounded by a Ti mash coated with a photoactive TiO_2 film, which was directly grown on the metal Ti mesh by Plasma Electrolytic Oxidation (PEO) at 150 V in 1.5 M H_2SO_4 [3]. The so prepared TiO_2 film, characterized by XRD, SEM and UV-vis DRS, consists of a 45% anatase and 55% rutile mixture and has a sponge-like morphology with a pore diameter of ca. 400 nm (Fig.1) and a band gap of ca. 3.06 eV. The PEC reactor operates at 4 V potential drop between the TiO_2 coated mesh (photoanode) and the body of the reactor (cathode), in 5 mM KCl as electrolyte solution containing an initial ammonia concentration of 20 ppm. The photocatalytic tests were performed by recirculating 3 L of solution through the reactor at 120 L h^{-1} flow rate. Under this condition, 71% ammonia conversion (X_{NH_3}) was attained after 8 h irradiation with a selectivity to N_2 (S_{N_2}) of 61% and to NO_3^- of 39%. Full X_{NH_3} was reached after 12 h with a S_{N_2} up to 67% (Fig.1). Nitrite was produced within the first 6 h irradiation and then fully converted into nitrate. Increasing the recirculation flow rate up to 350 L h^{-1} led to a decrease of both X_{NH_3} (56%) and S_{N_2} (44%) after 8 h irradiation, because of the lower residence time. In all tests the photocurrent was ca. 150 mA. In order to simulate the NH_3 production in a fish tank an additional test was performed by initially introducing in the system only half of the volume (1.5 L) of pure electrolyte solution, followed by the dropwise addition of 1.5 L of a 4 ppm NH_3 containing solution, in 8 h. The NH_3 and nitrite concentration remained always below the detection limit of the ion chromatography analysis (i.e., ca. 100% X_{NH_3}) and S_{N_2} of ca. 44%. In conclusion, this work demonstrates that this PEC reactor could be employed, after a proper scale-up, as a remediation system for NH_3 abatement in water.

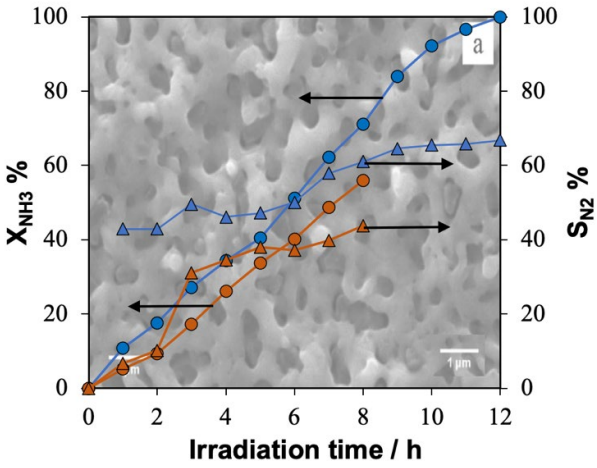

Figure 1: Effect of flow rate (120 L/h blue lines and 350 L/h orange lines) on X_{NH3} (♦) and S_{N2} (▲). The graph background shows the SEM image of TiO_2

Acknowledgement
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Smart Agri-Cosmetic: from artichoke wastes to the hair salon

L. Longo[a], E. Ghedini[a], G. Grillo[b], S. Tabasso[b], G. Cravotto[b], I. R. Redovnikovic[c], M. Signoretto[a]

[a] Dep. of Molecular Sciences and Nanosystems, Ca' Foscari University, Via Torino 155, 30172 Venice, Italy. [b] Dip. di Scienza e Tecnologia del Farmaco, University of Turin, Via P. Giuria 9, Turin, 10235, Italy.[c] Dep. of Biochemical Engineering, University of Zagreb, Pierottojeva ulica 6, Zagreb, 10000, Croatia.

The saving, reuse, and recycling of industrial residues, that come to new life as potential resources or raw materials, are the key paradigms of the Circular Economy concept. Since 2015, the European Union has been moving toward this economic transition in order to support the climatic, economic, and social challenges. In recent years, even in the cosmetic field, more and more attention has been paid to these topics by both developers and consumers and the major market cosmetic players have been moving in this direction for several years. L'Oréal was a pioneer who launched the "Sharing Beauty with All" Program in 2013; Esteé Lauder, on the other hand, announced the goal of ensuring that, by 2025, from 75 to 100 percent of its packaging will be recyclable, reusable, or recoverable. This is fully consistent with the trend of the natural cosmetics market that currently is showing exponential growth with a value, forecasted for 2025, of 45 million euros [1]. The formulation of completely sustainable cosmetic products involves not only the use of recyclable packaging but also the careful choice of raw materials and process parameters. In this context, agri-food biomasses represent a promising source of ingredients. The goal of this project, financed by the European Social Fund, was the optimization of an effective production chain to transform artichoke wastes into valuable cosmetic products. Enabling technologies, such as Ultrasound (US) and Microwaves (MW) were compared and combined to improve the sustainability of the process by reducing the extraction time while increasing the yields of bioactives (phenolic compounds and polysaccharides). Artichoke by-products supplied by the merchants of Rialto Market in Venice were used as raw material for US and MW assisted extractions under different conditions, and the impact of these technologies on phenolic content, antioxidant capacity and polysaccharides yields was evaluated. The extracts were then used as active ingredients and raw materials for the formulation of cosmetic products for the hair care sector. The use of biomass derived functional ingredients involves several critical issues concerning their complexity in terms of composition and physical features (color, granulometry, smell). The bioactive metabolites effectiveness was maximized using Hi-Tech protocols, in order to assure the optimal dosing, bioavailability and penetration of functional ingredients by the exploitation of the Drug Delivery Systems technology (DDS, controlled release of an active molecule). A hybrid organic-inorganic gel network was used as matrix and the formulation was optimized by adding the appropriate rheological modifiers and excipients. The reagents ratio and the synthetic parameters were optimized in order to adapt the formulation protocol to the biomass extracts with the aim to obtain a performing final product, pleasant for the customers and with modulable final texture. The products features were analyzed in depth to evaluate stability, efficacy and skin compatibility; *in vivo* tests are currently ongoing by hair care experts. The preliminary results are very promising and demonstrate that technology, biomass valorization and partnerships between research and market worlds are winning and concrete strategies to promote the innovation in the name of sustainability.

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MO_x-doped WO_3/TiO_2 catalysts for removal of NO_x by NH_3-SCR

C. Migliore[1], L. Consentino[1], L. F. Liotta[1], G. Pantaleo[1]

[1] Institute for the Study of Nanostructured Materials (ISMN)-CNR, via Ugo La Malfa, 153, 90146, Palermo, Italy

Nitrogen oxides NO_x (NO and NO_2) produced from mobile and stationary sources are responsible of many serious environmental issues (photochemical smog, acid rain and ozone depletion) and damages to the human health [1-4]. Selective catalytic reduction (SCR) by ammonia over V_2O_5-WO_3/TiO_2 based catalysts is one of the most effective methods used for removal of NO_x. However, these systems are effective in a relatively narrow range of temperature (between ~250-400 °C) and the N_2 selectivity starts to decrease above 300 °C [5,6]. Since many years, CeO_2 has attracted a lot of attention in catalytic field, especially in automotive applications, due to the excellent redox properties and oxygen storage capacity. Ceria, in addition, contrary to V_2O_5 whose toxicity is known, is a non- toxic compound. MnOx-TiO_2 based catalysts have been reported to be active and selective in NO SCR at T <150 °C [7,8]. The excellent redox property of Mn-based catalysts could greatly facilitate the low-temperature SCR activity [9].
In this work, with the purpose to enlarge the operative window at T <250 °C and improve the catalytic performance with respect to a conventional V_2O_5-WO_3/TiO_2 reference, a series of MO_x-WO_3/TiO_2 catalysts (M = Ce, Mn), were synthesized by wetness impregnation method of the metal precursors, over commercial TiO_2. The morphological, structural and redox properties of the prepared samples were investigated. The catalytic activity was evaluated in NO by NH_3 SCR tests, working at NO concentration typical of a diesel engine exhaust gas.

Acknowledgement. The project TECBIA "Tecnologie a Basso Impatto Ambientale per la produzione di energia sui mezzi navali" (Progetto n. F.090041/01/X36 –CUP B98I17000680008)" and the project PON ARS01_00334 – NAUSICA "NAvi efficienti tramite l'Utilizzo di Soluzioni tecnologiche Innovative e low CArbon" are acknowledged for financial support.

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Control of Properties of PPO films by Planar Orientation of Nanoporous-Crystalline and Co-crystalline Phases

*Baku Nagendra, Manohar Golla, Christophe Daniel, Paola Rizzo, Gaetano Guerra**

University of Salerno, Chemistry and Biology Department, Via Giovanni Paolo II 132, 84084 Fisciano (SA),

Properties of the semicrystalline polymers are strongly dependent on chain axis orientation and, as a consequence, there is a significant interest in the control of the chain/crystalline phase orientation in polymer films. The one-dimensional (1D) nature of the linear polymer chain makes it possible to obtain different kinds of orientations (Figure 1), like for instance with chain axes parallel ($c_{//}$) or perpendicular ($c_{\perp}$) with respect to the polymer film plane.[1] These oriented polymer films have been shown anisotropic properties, like an electrical, optical, magnetic, barrier, etc., possibly suitable for advanced material applications.[2]

Development of microporous polymers with the combination of molecular recognition, separation, and storage features is considered to be a challenging task. In 2011, nanoporous-crystalline (NC) phases of poly(2,6-dimethyl-1,4-phenylene) oxide (PPO) were discovered,[3] which have a unique characteristic of selective and fast kinetics of uptake of organic molecules, from both vapor phases and dilute aqueous solutions.

Recently, it was also reported that, by using suitable processing conditions, this polymer could exhibit co-crystalline (CC) and NC phases with two kinds of planar orientations ($c_{//}$ and $c_{\perp}$).[4,5] The control of planar orientation allows to get control of guest diffusivity and stability as well as of transparency of PPO films.[6]

The combination of control of functional properties with the excellent dimensional and mechanical properties of PPO allows anticipating new possible applications of semicrystalline PPO films.

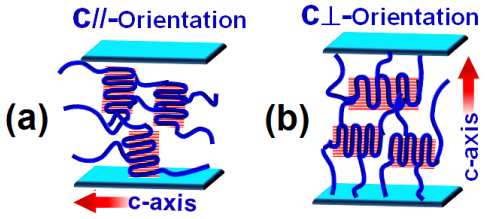

Figure 1. Schematic illustration of (a) c-parallel, $c_{//}$, and (b) c-perpendicular, $c_{\perp}$, chain orientations with respect to the polymer film plan.

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Recent progress on light responsive smart materials for the development of artificial muscles

D. Natali[a], D. Martella[a,b], S. Nocentini[a,b], D. S. Wiersma[a,b,c], C. Parmeggiani[a,b,d]

[a]European Laboratory for Non-linear Spectroscopy, via Nello Carrara 1, Sesto Fiorentino (FI)
[b]Istituto Nazionale di Ricerca Metrologica (INRiM), Strada delle Cacce 91, Torino
[c]Department of Physics and Astronomy, University of Florence, Via Sansone 1, Sesto Fiorentino (FI)
[d]Department of Chemistry "Ugo Schiff", University of Florence, via della Lastruccia 3, Sesto Fiorentino (FI)

Polymers able to generate a response to an external stimulus are commonly called smart materials. The possibility to remotely control them allow for the development of artificial muscles to be used in biomedical and soft-robotics applications[1]. Among smart materials, liquid Crystal Networks (LCNs) can be used as photoresponsive polymer. The light actuation mechanism can be obtained including in the LCN matrix an organic dye and taking advantage of the photothermal effect: under irradiation the dye is able to absorb the light and to get into vibrational relaxation thus provoking an increase in temperature that allow the LCN to change its molecular structure and shape[2].
Adding different kinds of dyes, the response of the material can be easily modulated, playing with the light wavelength and power, thus allowing the selective activation of different materials. It is worth noting the importance of this aspect since in the field of biomedicine or soft-robotics a selective photoresponse could lead to a great raising in the efficiency of the devices.
In this presentation, we will show the characterization of light responsive LCN containing different dye as shown in Figure 1. Dyes have been chosen to have different maximum wavelength absorption and molar absorption coefficient: in the former case the response will depend directly from the color of the light, while in the latter the material will exhibit a different behavior depending on the light intensity.
We will focus on LCNs actuation mechanism and their possible applications such as contracting materials to build up microrobotic systems.

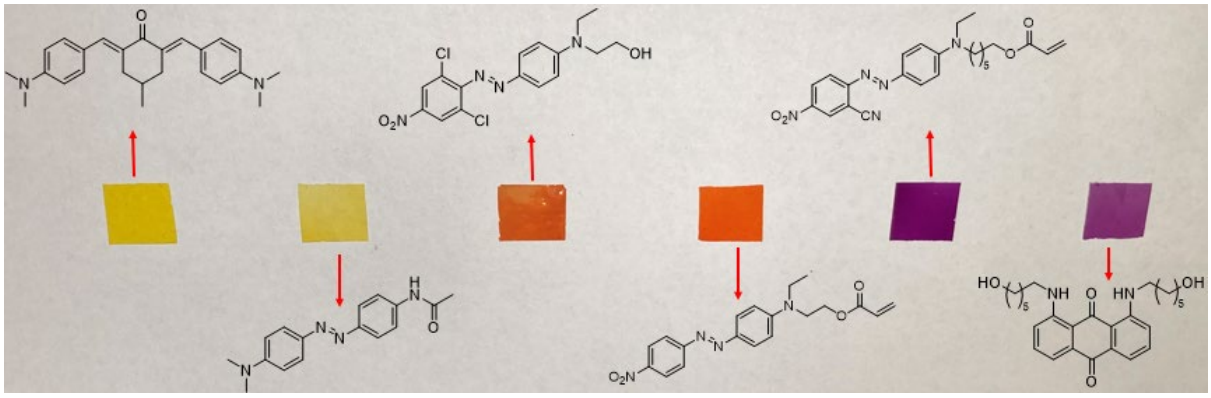

Figure 1: Picture of different LCN films and structure of dispersed dye.

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Microwave-Assisted Silver Nanoparticles Decoration of Polymer-Based Graphene Derivatives as a Potential Antibacterial Agent

A. Nicosia[a], F. Vento[a], A. L. Pellegrino[a], V. Ranc[b], A. Piperno[c], A. Mazzaglia[d], G. De Guidi[a], and P. Mineo[a]

[a] Department of Chemical Sciences, University of Catania, V.le A. Doria 6, 95125, Catania, Italy; [b] Regional Centre of Advanced Technologies and Materials, Palacký University Olomouc, Šlechtitelů 11, Olomouc, 78371, Czech Republic;[c] Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, V.le F. Stagno d'Alcontres 31, 98166 Messina, Italy; [d] CNR-ISMN, Istituto per lo Studio dei Materiali Nanostrutturati, V. le F. Stagno d'Alcontres 31, 98166, Messina, Italy.

The polymer-based materials are ubiquitously applied as structural materials for everyday use objects and value-added devices: from kids toys manufacturing to biomedical devices (such as catheters, ureteral stents and prosthesis). Due to bacterial surface contaminations, severe infections could occur, especially through the application of invasive biomedical devices. Usually, to provide a long-term antibacterial effect besides the preparatory materials sterilization [1], low-molecular-weight organic molecules are used as antimicrobial agents. The application of such molecules occurs through spray coating techniques or blend with polymer matrix [2], but their low adhesiveness onto the substrate resulted in leakage in the environment, where they bioaccumulate and act as endocrine disruptors [3]. Their adverse effects have led to the ban on some of them [4].

Hybrid nanocomposites obtained by decorating graphene-based materials with silver nanoparticles (AgNPs) have received increasing attention due to their antimicrobial activity. However, the complex synthetic methods for their preparation have limited practical applications.

This study shows the synthesis of novel NanoHybrid Systems based on graphene, polymer, and AgNPs (namely NanoHy-GPS) through a straightforward microwave-assisted synthetic approach, free of reductants and surfactants [5].

The polymer moiety plays a crucial role since it assures the coating layer/substrate compatibility, making the platform easily adaptable for a specific substrate. Thus, the synthetic strategy was chosen to ensure the interchangeability of the polymer moieties. The loading of AgNPs (from 5% to 87 %) was tuned by adjusting the Silver salt amount used during the microwave-assisted reaction. Consequently, homogeneously distributed AgNPs (ranging from 5 to 12 nm) on the polymer-graphene nanosystem were obtained. Interestingly, microwave irradiation partially restored the graphene sp^2 network without damaging ester bonds.

The structure, morphology and chemical composition of NanoHy-GPS and of its precursors were characterized through several techniques (UV-Vis spectroscopy, thermal analysis, DLS, field emission scanning electron microscopy, EDX, AFM, HRTEM). Finally, a preliminary qualitative assay to assess the antibacterial properties of NanoHy-GPS against a typical bacterial population present on common hand-contacted surfaces has been performed. The data evidenced a significant reduction of bacterias colonies spreading.

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Preparation of hydrophobic porous membranes for membrane distillation using pore forming agents

Marcello Pagliero[a], *Antonio Comite*[a], *Camilla Costa*[a], *Ilaria Rizzardi*[a]

[a] *membrane&membrane research group, Department of Chemistry and Industrial Chemistry, Università degli Studi di Genova, Via Dodecaneso 31, 16146, Genova, Italy.*

Introduction

Membrane distillation (MD) requires membranes with high hydrophobicity and large porosity in order to maintain both the separation ability and high permeate flux of the process [1]. One possible approach to improve the membrane porosity is to use pore forming agents [2] which are water soluble molecules that modify the phase separation process altering the membrane morphology during its formation.

Materials and methods

Unsupported flat sheet membranes were prepared exploiting the nonsolvent induced phase separation technique starting with a homogeneous polyvinylidene fluoride/N,N-dimethylformamide solution. Three different pore forming agents were used to tune the membrane structure. In particular, two polyethylene glycols (PEG) with different molecular weight (400 and 6000 Da) and an inorganic salt (LiCl) were tested. The MD performance was evaluated in direct contact mode using both deionized water and a concentrated NaCl solution as feeds.

Results

The type of additive used, as well as its concentration, deeply modified the membrane structure. In general, the addition of pore forming agents allowed to create membranes with higher overall porosity and smaller pore size but also resulted in lower water contact angles.

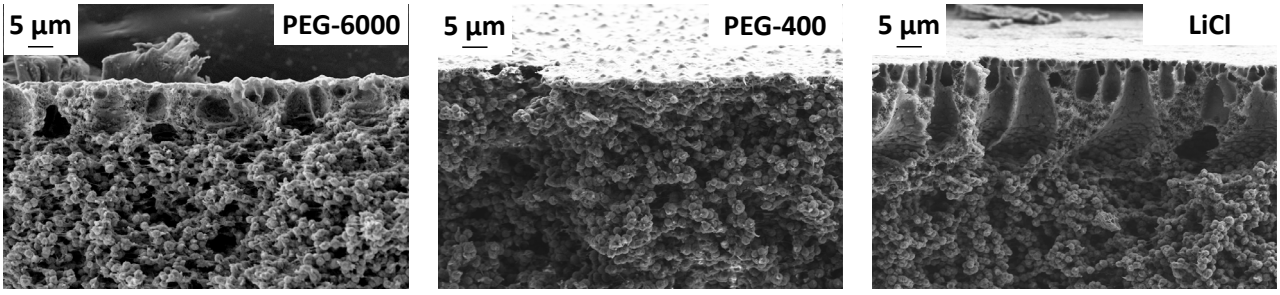

Figure 1: Cross section of membranes prepared using different pore forming agents: PEG-6000, PEG-400 and LiCl

In particular, using the two PEGs both symmetric globular membranes and asymmetric ones were obtained by tuning the additive and PVDF concentrations while, with each tested concentration, LiCl increased the precipitation rate of the dope solution creating a fingerlike layer under the surface skin of the membrane.

The MD tests were performed by means of direct contact MD operation mode. The membranes with larger pores provided the higher fluxes when deionized water was used but during the tests with the NaCl solution suffered different grades of flooding that reduced both the distillate flux and the salt rejection.

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Advanced porous frameworks: stimuli-responsive gas adsorption and fast scintillating materials for ionizing radiation detection

Jacopo Perego[a], Charl X. Bezuidenhout[a], Silvia Bracco[a], Angiolina Comotti[a] and Piero Sozzani[a]

[a] *University of Milano-Bicocca, Department of Materials Science, Milan, Italy*

Porous organic frameworks (PAFs) and Metal-organic frameworks (MOFs) were extensively studied in the past 20 years, widening the landscape of microporous materials.
Responsive porous frameworks can be manipulated by means of external stimuli such as applied electric field or light irradiation, thus controlling their textural properties at will. Molecular photoswitches were co-polymerized with tetraphenylmethane generating 3D PAFs with high surface area (up to 4800 m^2/g) and photo-responsive properties that quantitatively switch between stable and metastable state under U.V. light irradiation[1]. The localized and reversible photoisomerization reaction modified the bulk adsorptive properties of the porous materials with a 20% modulation of the adsorption capacity. These materials can be engineered to provide "on demand" adsorption properties for gas separation and gas storage/release.
Scintillating materials are widely employed in high-energy particles detection and medical imaging. Innovative composite scintillators with high light yield and fast response time were developed embedding luminescent MOFs in a polymer matrix[2]. Highly emissive MOFs nanocrystals (ZrDPA) were synthetized by the assembly of 9,10-bis(4-carboxyphenyl)anthracene (DPA) and zirconium oxo-hydroxy cluster and dispersed in polymer matrixes to obtain self-standing monoliths. The MOF/polymer composites showed outstanding radioluminescence and scintillating properties with high light yields and scintillation rise time of ~ 50 ps, making them suitable for application in detectors for time-of-flight positron emission tomography (TOF-PET).

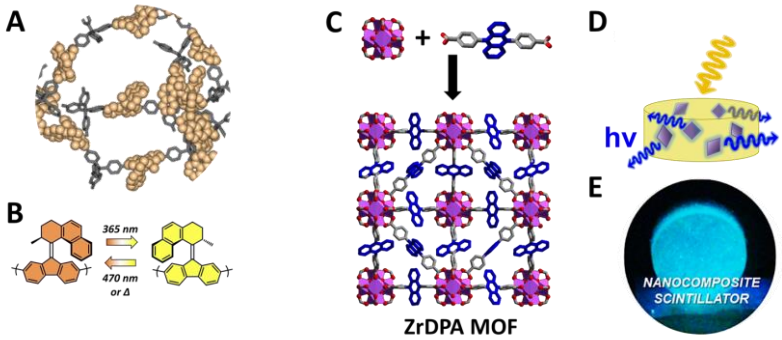

Figure 1. A) Sketch of the amorphous structure of PAF with installed photoswitching moieties. B) Photoisomerization between the stable (orange) and metastable state (yellow) of the installed photoswitches. C) $Zr_6O_4(OH)_4(COO^-)_{12}$ cluster (purple), DPA ligand (the anthracene moiety is highlighted in blue) and face-centered cubic structure of ZrDPA MOF. D) MOF/polymer composite and schematic representation of the scintillation process. E) Digital image of MOF/polymer composite under X-ray irradiation.

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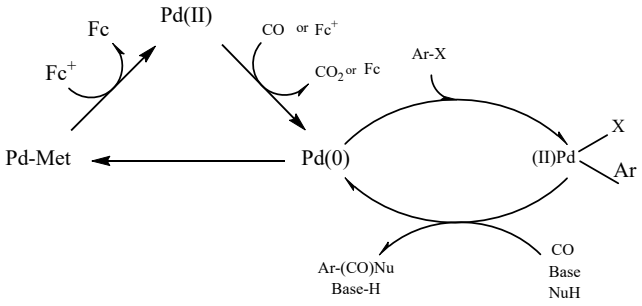
New Palladium-Based Catalytic System for the Sustainable Synthesis of Esters

Luca Pietrobon[a], Andrea Vavasori[a], Lucio Ronchin[a]*

[a] *Department of Molecular Science and Nanosystems, Ca' Foscari University Venice, Scientific Campus, via Torino 155, 30172 Venezia-Italy*

The derivatives of carboxylic acids, in particular esters and amides, are a starting material for the production of a wide range of bulk and fine chemicals, such as: polymers, pharmaceuticals, perfumes, etc.
In addition to classical organic syntheses, these molecules can be produced by carbonylation of olefins or aryl-alkyl halides.
Typically, these reactions are obtained through the use of palladium-based homogeneous catalysts[1].
The carbonylation of aryl halides has a great potential from the synthetic point of view but has productivity not suitable for an industrial application (TON 100-10000) especially when compared to the Heck and Suzuki reactions (TON 100'000-1'000'000).
One of the main problems with this type of homogeneous catalysis is deactivation due to agglomeration and precipitation of Pd-metal, which is less active for catalysis.
Taking as a model reaction the methoxycarbonylation of iodobenzene, catalyzed by [$PdCl_2$(Xantphos)] we studied the optimization of the reaction parameters and the influence of some additives, with the aim to avoid the catalyst deactivation.
In particular have been observed positive effects on the productivity by adding the redox couple Ferrocene/Ferricinium as cocatalyst which allow to obtain TOF over 300'000 h^{-1} without an evident formation of palladium black.



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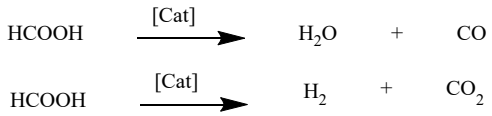
Sustainable Generation of CO from Formic Acid for Carbonylation of Alkenes

Luca Pietrobon[a], Andrea Vavasori[a], Lucio Ronchin[a]*

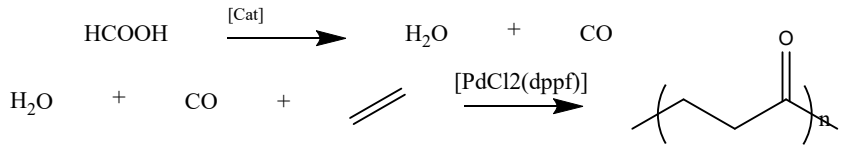
[a] *Department of Molecular Science and Nanosystems, Ca' Foscari University Venice, Scientific Campus, via Torino 155, 30172 Venezia-Italy*

The use of high-pressure carbon monoxide, due to its toxicity and flammability, requires specific measures to work safely. Recently the academic world, in order to overcome these problems, is focusing its attention on the study of carbonylation reactions obtained through the use of carbon monoxide surrogates [1].
From an "atom economy" point of view, formic acid, which can be obtained by catalytic hydrogenation of carbon dioxide[2] or by fermentation of agricultural waste material, is one of the best candidates for carbon monoxide generation.
Although formic acid can be considered as a storage of carbon monoxide, one of the main problems encountered in the use of this surrogate is its non-specific decomposition in the presence of transition metals (scheme 1)



Scheme 1

It is well known that formic acid can be dehydrated, and thus release CO, by the use of strong mineral acids such as concentrated sulfuric acid [3].
The challenge is that with the progression of the reaction, the CO release becomes less and less efficient due to the dilution of the sulfuric acid.
Here we present the use of heterogeneous acid catalysts able to allow the release of carbon monoxide from HCOOH. Such a system allows the acid catalyst to be recovered by simple filtration and reused, after reactivation, without significant loss in activity.
This system has also been successfully applied to the synthesis of poly(1-oxo-trimethylene) oligomers from ethylene and carbon monoxide catalysed by the [PdCl2(dppf)] complex [4]. Scheme(2)



Scheme 2

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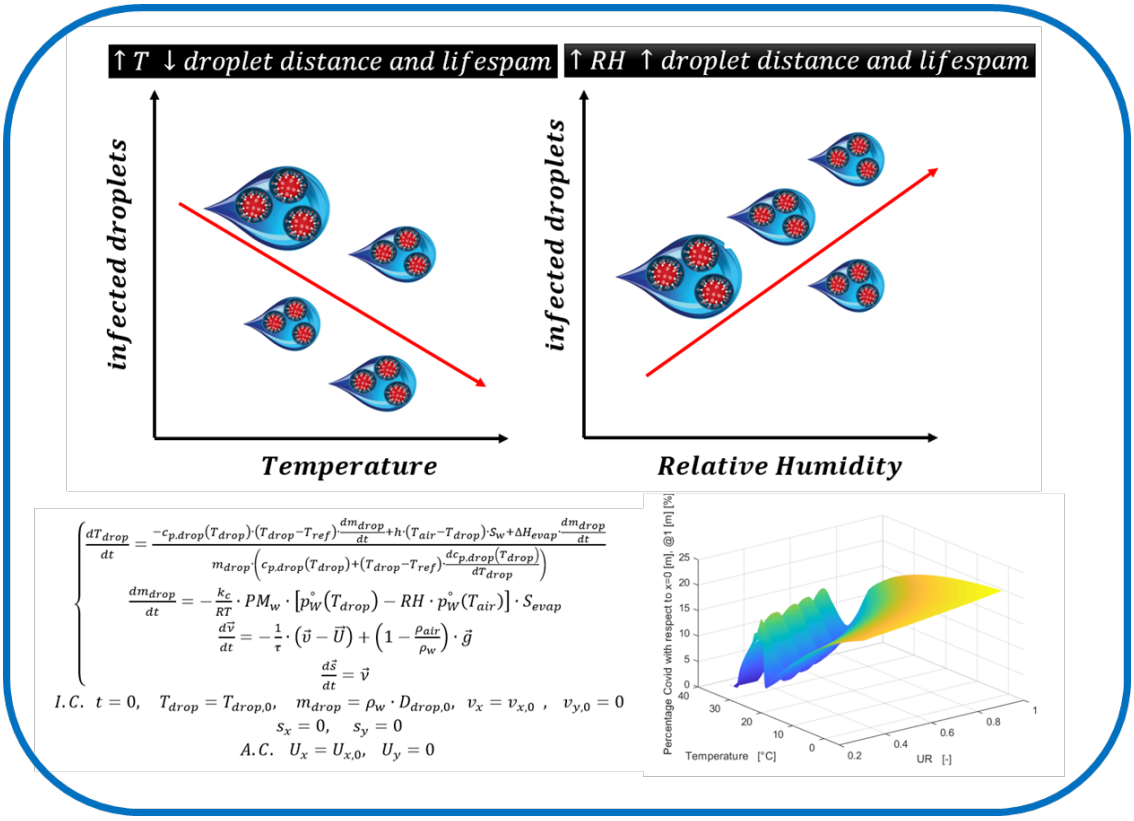
Influence of Environmental Parameters on the Droplet-Mediated Spread of Respiratory Viruses as SARS-CoV-2

Carlo Pirola[a], Sabrina Copelli[b]

[a] Università degli Studi di Milano, Dipartimento di Chimica; via Golgi, 19 - 20133 Milano (Italy); [b] Università degli Studi dell'Insubria, Dipartimento di Scienza e Alta Tecnologia; via Valleggio 9 – 22100 Como (Italy)

A clear seasonality has been shown for many respiratory viruses whose transmission relies on droplets released from humans, including SARS-CoV-2. A better understanding of the determinants of virus transmission between humans would help identify optimal epidemiological strategies to reduce the SARS-CoV-2 spread [1], without an exorbitant impact on the economy.
Basing on the observation that the pandemic is dependent by external temperature (Tair), relative humidity (RH) and air speed, we modelled the effect of these parameters on the diffusion of respiratory droplets. A lagrangian model of droplet evaporation/settling was used to assess the lifespan of respiratory droplets as a function of Tair, RH and air velocity. In the presence of low Tair and high RH (independently on the air velocity considered), both the distance covered by the droplets and the percentage of virus were significantly higher than in the presence of medium-high Tair and medium-low RH. These data suggest that the minimum social distances recommended to minimize the spread of virus could be adapted to outdoor climate conditions and reduced by modulating Tair, RH and air velocity of indoor environments.
The study reported in this paper is adaptable to any transmission of viruses via human saliva. However, given the ongoing health emergency, an analysis will be carried out with respect to the particular trend of COVID-19 infections,



$$\begin{cases} \frac{dT_{drop}}{dt} = \frac{-c_{p,drop}(T_{drop})\cdot(T_{drop}-T_{ref})\cdot\frac{dm_{drop}}{dt}+h\cdot(T_{air}-T_{drop})\cdot S_w+\Delta H_{evap}\cdot\frac{dm_{drop}}{dt}}{m_{drop}\cdot\left(c_{p,drop}(T_{drop})+(T_{drop}-T_{ref})\cdot\frac{dc_{p,drop}(T_{drop})}{dT_{drop}}\right)} \\ \frac{dm_{drop}}{dt} = -\frac{k_c}{RT}\cdot PM_w\cdot\left[p_W^{\circ}(T_{drop})-RH\cdot p_W^{\circ}(T_{air})\right]\cdot S_{evap} \\ \frac{d\vec{v}}{dt} = -\frac{1}{\tau}\cdot(\vec{v}-\vec{U})+\left(1-\frac{\rho_{air}}{\rho_w}\right)\cdot\vec{g} \\ \frac{d\vec{s}}{dt} = \vec{v} \end{cases}$$

$$I.C.\ \ t=0,\quad T_{drop}=T_{drop,0},\quad m_{drop}=\rho_w\cdot D_{drop,0},\quad v_x=v_{x,0}\ ,\quad v_{y,0}=0$$
$$s_x=0,\quad s_y=0$$
$$A.C.\ \ U_x=U_{x,0},\quad U_y=0$$

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$Mo/Ce_{1-x}Ni_xO_{2-y}$ as Dry Reforming Catalyst for application in solid oxide fuel cell anodes

Marco Pizzolato[a], Michela Signoretto[a], Federica Menegazzo[a], Linda Barelli[b], Alessandro Di Michele[c], Federico Gallorini[d], Andrea Ottaviano[d], Giuseppe Cruciani[e]

[a] CATMAT Lab, Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia and INSTM RU of Venice, via Torino 155, Venezia Mestre [b] Dipartimento di Ingegneria, Università di Perugia, Via G. Duranti 1/A4, Perugia [c] Dipartimento di fisica e Geologia, Università di Perugia, Via Pascoli 1, Perugia [d] VGA s.r.l., Via Ugo Foscolo,1 San Nicolò di Celle [e] Dipartimento di Fisica e Scienze della Terra, Università di Ferrara, Via Saragat 1, Ferrara

The solid oxide fuel cells (SOFC) technology has been considered as an attractive energy conversion system. It has several advantages such as high efficiency, relatively low sensitivity to impurities, and possibility for operation with an internal reformer [1,2]. In the case of the direct internal reforming solid oxide fuel cell (DIR-SOFC), the complexity and costs of the fuel cell system are reduced since the fuels can be fed straight to the anode side of SOFC and reformed to H_2 without the use of an external reformer. In addition, the conversion of these fuels at the anode side can be promoted due to the H_2 consumption by the electrochemical reaction, leading to high conversions and high efficiency [3].

The Dry reforming reaction is a reaction which involves the hydrocarbons reforming using CO_2 to produce Syngas (H_2+CO) [4]. This reaction compared to other reforming reactions has two important aspects that must be considered in order to grasp efficiently the possibilities as well as the restrictions of this process. Interactions between carbon dioxide and methane is of course a priority, however, one of the most limiting aspects of the dry reforming reaction is the formation of carbon [5-7]. A catalyst for this reaction must possess good activity and resilience to coke deposition ensuring catalyst's stability.

Here we present Ni-doped cerium-based samples promoted with molybdenum as efficient catalysts for dry reforming reaction that could be applied as reforming layer in SOFC where Ni is the active phase of the catalyst, Ce acts as support and Mo has the role to decrease coke deposition on catalyst surface. The optimum catalyst's formulation has been studied using different synthetic approaches as co-precipitation, sol-gel, and impregnation: particularly, the compatibility with Yttria-Stabilized Zirconia (YSZ) anodes has been taken into account, with the aim to obtain a catalyst with good adhesion and similar thermic dilatation coefficient of YSZ. To evaluate the desired morphological and structural features of the as prepared materials several techniques have been employed like TPR, N_2 physisorption, XRD, SEM, CO chemisorption both on fresh and spent catalysts. The catalysts were preliminary tested in the Methane Dry Reforming Reaction, choosing reaction conditions consistent with SOFC application (CH_4/CO_2 ratio 1:1; 600-700°C). The best or more performant catalysts will be used as reforming layers for YSZ SOFC anodes.

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Renewable resources for the synthesis of novel ester biofuels employed as diesel blendstocks

Claudia Antonetti[a], Nicola Di Fidio[a], Stefano Frigo[b], Domenico Licursi[a], Rosaria Lorè[a], Marco Martinelli[a], Luca Mussi[a], Gianluca Pasini[b], Anna Maria Raspolli Galletti[a]

[a] Dipartimento di Chimica e Chimica Industriale - Università di Pisa, Italy. [b]Dipartimento di Ingegneria dell'Energia, dei Sistemi, del Territorio e delle Costruzioni – Università di Pisa, Italy

In these last years increasing attention has been devoted to biofuels, due to the novel regulations requiring the improvement of renewables in fuel composition. The addition of low net-carbon biofuels reduces the carbon footprint of Diesel combustion and can significantly improve the characteristics of both the engine performances and combustion emissions. Biofuels are forecast to grow more than 70 percent with increasing demand for lower-carbon liquid fuels and technology advancements that reduce costs and land-use, while global Diesel demand is forecast to have a significant growth through 2040, becoming the single largest liquid fuel segment [1]. The sustainability of the adoption of novel advanced biofuels is strictly related to the characteristics of the starting biomass as well as to the feasibility of the conversion process. Products obtained from waste or not edible cheap biomasses with a simple, high yield process represent effective renewable components of the fuel. In this perspective two different reactions have been optimized: the direct butanolysis of biomass to butyl levulinate (BL) [2] and the hydrogenation of hexanoic acid obtained from biomass anaerobic fermentation to give hexanol/hexyl hexanoate (HeOH/HeHe).

BL was obtained by one-pot butanolysis of various feedstocks having low or negative value (such as defatted cardoon, giant reed, papermill wastes) employing *n*-butanol as green reagent/reaction medium, very dilute proton acid as a homogeneous catalyst and different heating systems. Significant optimization of the reaction conditions has been carried out starting from the above raw or waste biomasses: under the optimized reaction conditions yields higher than 40 mol %, evaluated respect to the units of glucose in the starting materials, were reached, while the formation of dibutyl ether can be suppressed. Remarkably, these results were analogous to the best ones obtained under the same reaction conditions in the butanolysis of a pure valuable substrate as microcrystalline cellulose. The solid residue recovered from the alcoholysis has been characterized and proposed for different exploitation routes in the context of a more sustainable and integrated process.

HeOH/HeHe mixtures can be obtained with tunable composition and high selectivity by hydrogenation of bio-hexanoic acid. This research was performed in the framework of the PRIN 2017 "VISION" project, devoted to the exploitation of levulinic acid and carboxylate platforms [3]. Commercial Re/C resulted an active catalytic system whose selectivity and activity were tailored by changing the main reaction conditions, as hydrogen pressure, temperature and reaction time.

The reaction products obtained in the two processes were tested as effective renewable components in a mixture with Diesel fuel in a small single-cylinder air-cooled Diesel engine, evaluating the performances of different blend compositions [4]. The obtained results, compared with those obtained fuelling the engine with a conventional Diesel fuel, confirmed the significant potentiality of these novel mixtures to reduce the emissions of particulate without increasing NO_x emissions or worsening engine performances.

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NIR squaraine dyes for cell bilayer bioimaging: a structure-activity investigation

G. Renno,[a] M. Giordano,[a] N. Barbero,[a] P. Quagliotto,[a] G. Cravotto[b], G. Viscardi,[a] A. Fin[b]

[a] *Department of Chemistry, University of Torino, Torino, Via Pietro Giuria 7 10125, (Italy)*
[b] *Department of Drug Science and Technology, University of Torino, Torino 10125, Via Pietro Giuria 9, (Italy)*

Near-infrared (NIR) emissive probes have recently attracted an increasing interest as stain of cell bilayer membranes.[1] Membrane fluidity, polarization, as well as the specific interactions occurring among phospholipids, proteins and channels, are important to shed light on crucial biochemical pathways. In this context, small organic fluorescent compounds play a key role, allowing an accurate location within the membrane along with the possibility to fine-tune their optical features by simple structural modifications.[2] In particular, NIR probes exhibit remarkable brightness, deep tissue penetration and limited biological damage and autofluorescence.[3] Although several emitters have already been proposed for this purpose, a regular innovation in design of more performing probes is required.[4] A systematic structure-to-function study for novel bilayer membrane NIR probes could represent the starting point to precisely direct further investigations.

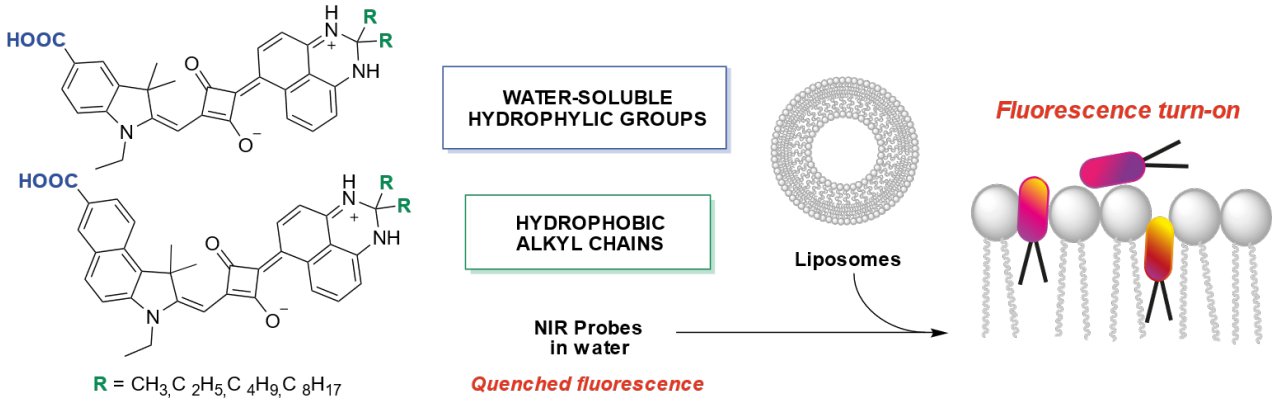

Figure. A schematic representation of the interaction between the synthesized NIR probes and liposomes.

In this work, novel asymmetric squaraines have been synthesized and characterized. A carboxylic group linked to an indolenine (or benzoindolenine) ring has been placed on one side, while on the opposite one a perimidine derivative has been decorated with alkyl chains of different length. The former improves the water solubility of the whole system, while the latter tunes the interaction of the probe with the lipophilic components of the cell membrane. The kinetic of the probes' intercalation inside the bilayers has been monitored by fluorescence spectroscopy. The effect of the membrane phase and fluidity on the interaction has been evaluated too, providing a complete analysis about the key structural motifs for the design of novel NIR probes.

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Nitrification process for ammonia removal in biological reactor aerated with porous polymeric membranes

Ilaria Rizzardi[a], Aldo Bottino[a], Gustavo Capannelli[a], Camilla Costa[a], Raffaella Firpo[a], Daniele Matteucci[b], Marcello Pagliero[a], Antonio Comite[a]

a) membrane&membrane Research Group, Department of Chemistry and Industrial Chemistry (DCCI), University of Genoa, Via Dodecaneso 31, 16146, Genova, Italy
b) SIMAM SpA, Via Cimabue, 60019 Senigallia (AN), Italy

Ammonia is a common pollutant present in industrial and domestic wastewater, whose high concentration in water streams can pose a danger to human health. For this reason the research is focused on development of methods for abatement of ammonia in wastewater [1]. To transform and remove the pollutants, biological treatment systems use the same tools as nature. In particular for ammonia removal, the nitrification-denitrification process converts nitrogen organic compounds to molecular nitrogen. Nitrification is the first step of the process and it consists of the aerobic oxidation of ammonia and nitrite by the action of autotrophic microorganisms [2]. Due to the aerobic nature of the microorganism the reaction is limited by the concentration of oxygen in the system. The low solubility of oxygen in water is the problem that we want to approach in this study. Dissolved oxygen concentration is affected by temperature, composition of wastewater feed, and interface surface available for the mass transfer. Porous membranes can be used as promoter of the contact between phases.

In this work membrane modules using hollow fiber polypropylene membrane were prepared and tested both in clean water and in biological systems to perform the nitrification process. The first step of the research had the purpose of obtaining the aeration curve to get the oxygen transfer coefficient (k_La) and the standard oxygen transfer efficiency (SOTE) in bubbleless and bubbling conditions. The test consisted in two steps: the first is the abatement of oxygen (with the addition of sodium sulphite) and the second is the aeration with the concentration of oxygen increasing until the concentration of saturation. Using the dataset obtained in the second part of the test k_La and SOTE were calculated and a comparison between the different systems prepared was done.

The second step of the research aimed at performing a nitrification process using membrane apparatus in order to remove the ammonia present in synthetic wastewater. These tests were made at 20°C in batch reactor using a membrane aerator and a biomass of oxidation active sludge plant. The water was prepared with high amount of ammonia (up to 500 ppm) and chlorides. The parameters detected during the research were pH, ammonia concentration, total suspended solids (TSS), anions concentration (chlorides, nitrites, nitrates, phosphates and sulfates) and COD. The amount of ammonia was determined with analysis kit and the amount of anion present in the system was detected using ion exchange chromatography.

The membrane diffusor prepared showed high efficiency at low flowrate in lab scale plant. During the nitrification ammonia was shot down and converted mainly into nitrites but also in nitrates. The oxygen concentration was not a limiting parameter using membrane system.

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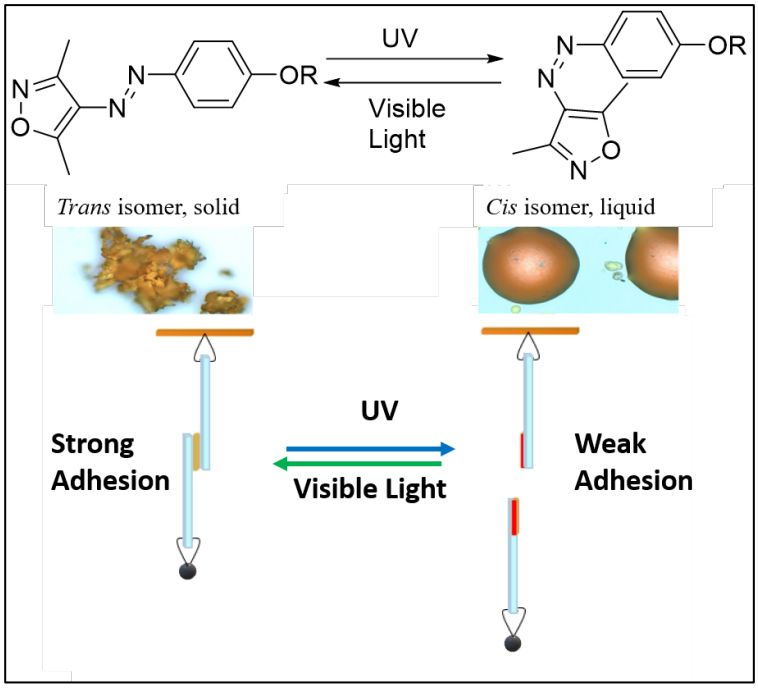
New photoresponsive adhesives containing arylazoisoxazoles

Ruggero Rossi[a], Daniele Martella[b,c], Benedetto Pizzo[d], Camilla Parmeggiani[a,b], Antonella Salvini[a]

[a]Department of Chemistry "Ugo Schiff", Università di Firenze, Sesto F.no, Italy; [b]European Laboratory for Non Linear Spectroscopy, Università di Firenze, Sesto F.no, Italy; [c]Istituto Nazionale di Ricerca Metrologica (INRiM), Torino, Italy; [d]Institute for the Bioeconomy (CNR-IBE), Italian National Research Council, Sesto F.no, Italy.



Finding new adhesive solutions results very interesting, expecially for those materials, such as glass, that do not allow common solutions. Here we present an alternative approach based on photoresponsive compounds which have been tested as photoreversible adhesives for glassy surfaces. The photochromic properties of those compounds have been investigated by UV-vis and ^{1}H-NMR spectroscopy measurements, while the adhesive properties have been measured through single lap shear tests.

Those adhesives contain an arilazoisoxazolic moiety which presents a photoisomerization around the N=N bond induced with UV light. This process can be reversed by irradiation with visible light. The new synthesized polymer showed stronger adhesive properties, compared to the corresponding monomer (adhesive strength of 2.79 MPa, 7 times greater than the arilazoisoxazole in literature [1]), and it was more photoresponsive and easier to spread on the joint. The synthesized poly-6-(4-((3,5-dimethylisoxazol-4-yl)diazenyl)phenoxy)hexyl didn't show a transition phase with the photoisomerization, but after the UV irradiation its adhesive strength drops by a 74 % that allows to easily debond the joint.

These preliminary results, open to the development of "green" adhesives, able to bond and debond two surfaces without the use of a solvent and facilitating the reversibility of the adhesion with the possibility of reusing the adhesive by UV-visible light irradiation cycles.

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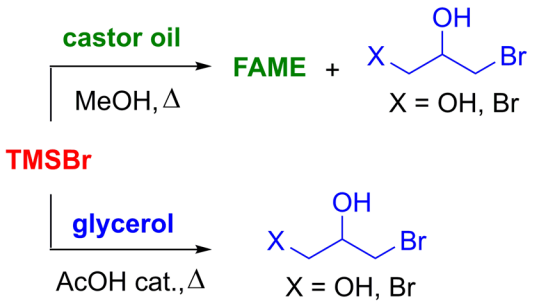
Bromoderivatives production by glycerol valorization

Donatella Giomi[a], Antonella Salvini[a], Jacopo Ceccarelli[a], Alberto Brandi[a]

[a]Department of Chemistry "Ugo Schiff" University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (Italy)

Glycerol is a byproduct in the biodiesel production from vegetable oils and for this reason it has become an interesting raw material for obtaining products of high added value. In fact, during the transesterification, ca. 10% by weight of the initial mass of triglycerides is transformed in glycerol (about 4 billion liters produced in 2020). Therefore, glycerol valorization becomes a crucial objective for the chemical industry.
Recently the selective transformation of glycerol to mono- and dichlorohydrins was obtained with trimethylchlorosilane (TMSCl), an excellent reagent to promote very efficiently the transesterification of exhausted vegetable oils and fats to Fatty Acid Methyl Esters (FAME) [1-3].
Now, trimethylbromosilane (TMSBr) has been studied as a reagent for the synthesis of bromohydrins from glycerol, also analyzing its effectiveness in the transesterification of triglycerides.
The production of α-monobromohydrin (1-MBH) and α,γ-dibromohydrin (1,3-DBH) from glycerol is an important process as bromo derivatives are important intermediates of fine chemistry [4]. In particular, 1,3-dibromoacetone could be obtained by 1,3-DBH for its use as a versatile building block for production of drugs, antibacterials or inhibitors. However, few methods to synthesize bromohydrins from glycerol have been reported in the literature exploiting the use of toxic or dangerous reagents as brominating agents (bromine, phosphorous and bromine, phosphorous tribromide, hydrobromic acid, trifuoroacetic anhydride and lithium bromide) or multi-step processes with dichlorohydrins as intermediates.
The results obtained in our laboratory show that TMSBr is a very efficient and selective reagent, more than TMSCl, in the direct, solvent-free conversion of glycerol into bromohydrins, leading selectively and in high yields to 1-MBH or 1,3-DBH by a careful choice of the reaction conditions [5]. Finally, TMSBr is a mediator able to provide triglycerides transesterification in good yields in acidic conditions with substrates leading to a homogeneous solution as castor oil.



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Direct synthesis of hydrogen peroxide in organic solvents: is the measure of the product still an issue?

Francesco Sandri[a], Mattia Danieli[a], Marco Zecca[a], Paolo Centomo[a]

[a] *Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1-I35131 Padova (Italy)*

The direct synthesis (DS) of hydrogen peroxide (HP) from dihydrogen and dioxygen, catalyzed by nanostructured palladium, has been intensively studied for thirty years now. Research in this field is thrusted by the demand for "green" oxidants to replace polluting ones, still used in several processes.[1] This calls for medium and small scale HP production which cannot be afforded by the current chemical technology (anthraquinone auto-oxidation process) and for this purpose the DS seems one of the most promising alternatives.[2]

The reaction involves the dissolution of H_2 and O_2 in a liquid phase, which generally contains an organic solvent such as methanol to increase the solubility of gases. This should be a reason of concern about the quantitative analysis of the HP produced during the catalytic test. According to the literature, this is measured with one of four main different methods: iodometric, cerimetric and permanganometric titrations and the UV-Vis detection of titanium oxysulfate. However, these methods were initially developed for the analysis of HP in purely aqueous solutions and organic substances such as the alcoholic co-solvent or other additives could interfere. Nevertheless, this question seems to be often overlooked in the literature.

To address this problem, several methanol solutions with different known HP concentration were analyzed with the above-mentioned methods and the results were compared to those expected.[3] Bromide ions and mineral acids, typically used as selectivity enhancers in the DS, were also added in different amounts to these solutions. The results highlight the differences of performance of these analytical methods as applied to actual DS reaction mixtures and provide a practical guideline to the choice of the best suited to the system under investigation. It was found that analytical errors can arise not only from too low or too high HP concentration, but also from the presence of halides and of suspended solids, formed by the mechanical degradation of the catalyst.

In particular, the results of iodometric titrations are strongly affected by the amount of acid in solution; the presence of bromide makes the identification of the end point of the titration very hard. Permanganometry is not recommended when organic solvents are present because they are oxidized too by MnO_4^-, leading to a high overestimation of the HP concentration. Cerimetric titration are apparently not affected by any interference, but it turns out to be not reliable for very diluted solutions. Conversely, UV-Vis detection using titanium oxysulfate appears very accurate over a wide range of HP concentrations: no chemical interference is observed, but light scattering produced by suspended solids invisible to the naked eye can lead to higher observed absorbance and overestimation of HP.

In conclusion, this investigation shows that attention must be paid to the choice of the analytical methods for the analysis of HP solutions obtained from the DS, since their responses can appreciably differ depending on the composition of the mixture.

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Innovative floatable O-g-C_3N_4 alginate spheres for water remediation under solar light

Claudia L. Bianchi,[a,b] Ermelinda Falletta,[a,b] Rhida Djellabi,[a] Anna Bruni,[a] Marta Sartirana[a]

[a] Department of Chemistry, University of Milan, via C. Golgi 19, 20133, Milan, Italy
b Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), via Giusti 9, 50121 Florence, Italy

In the last decades, the attention to environmental issues and the race to develop eco-friendly processes, has further attracted the field of research towards an inexpensive, simple, and reliable technology. A concerning global issue is freshwater scarcity mainly caused by leaking landfills, industrial waste, and sewage. In this regard, heterogeneous photocatalysis could offer a feasible solution to this problem aiming at the development of photoactive devices suitable for water remediation. Although TiO_2 is still the most used semiconductor due to its chemical and physical stability, good photoactivity and low cost, researchers are willing to replace it with new smart materials because of its suspected carcinogenic nature and limited activity under solar light[1]. Among them, g-C_3N_4 has promising features as photocatalyst for water-remediation considering its visible-light response, simple synthetic pathway, \\peculiar layered structure and cheap production cost[2]. To overcome problems related to the use of slurry systems for water purification, new floating substrates were employed to immobilize the photocatalyst. Since their closeness to water-surface, these devices can be fully irradiated by light source, better oxygenated, and easily recovered and reused[3]. Within this framework, synthetic polymers are commonly used as support, however their non-degradability has raised ecological concerns. Instead, an eco-friendly alternative can be the use of natural polymers, such as alginate, which derives from brown seaweeds and can be used for the immobilization of photocatalysts under safe and mild conditions[4]. In the present study, different methods were applied in order to synthesize floating alginates as support for O-doped g-C_3N_4 catalysts, whose activity was improved under visible light by doping with oxygen. These materials were deeply studied for photodegradation of rhodamine B, sodium diclofenac and isoproturon in water under solar light irradiation. Furthermore, floating photocatalyst were subjected to recycle test, in order to verify their activity and stability after several experiments.

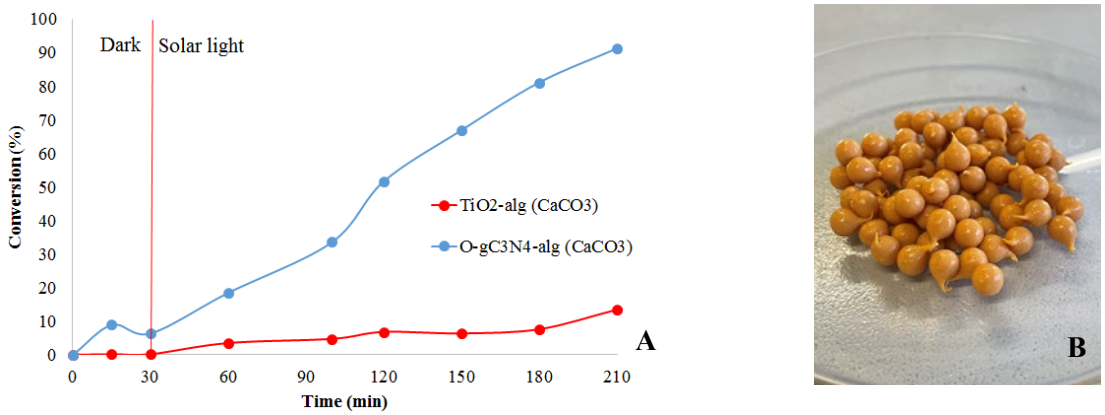

Figure: A: Photodegradation of rhodamine B under solar light using TiO_2 floating alginate spheres (TiO_2-alg ($CaCO_3$)) and O-g-C_3N_4 floating alginate spheres (O-gC_3N_4-alg ($CaCO_3$)). B: floating O-g-C_3N_4 floating alginate spheres.

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Reverse micelle synthesis of MnOx-TiO_2 nanoparticles and their remarkable catalytic activity in the selective catalytic reduction of NOx with NH_3 at both low temperature, and low Mn content.

Olimpia Tammaro[1], Barbara Bonelli[1], Ferenc Martinovic[1], Roberto Nasi[1], Gianfranco Dell'Agli[2], Paola Rivolo[1], Fabrizio Giorgis[1], Nicoletta Ditaranto[3], Fabio Deorsola[1], Serena Esposito[1]

[1] *Dipartimento di Scienza Applicata e Tecnologia (DISAT) and INSTM Unit of Torino-Politecnico, Corso Duca degli Abruzzi, 24, Politecnico di Torino, 10129, Torino, Italy.*
[2] *Dipartimento di Ingegneria Civile e Meccanica, Università degli Studi di Cassino e del Lazio Meridionale, Via G. Di Biasio 43, 03043 Cassino (FR)*
[3] *Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, via Orabona 4, 70125 Bari, Italy*

Nitrogen oxides are among the most dangerous by-products emitted by combustion engines and power plants [1]. Among different techniques used to reduce nitrogen oxides (NOx) emissions, the Selective Catalytic Reduction (SCR) is considered one of the most reliable and efficient method due to NO_x reduction efficiency, durable performance and reasonable costs. It allows converting NOx into nitrogen (and water) by introducing ammonia (or urea) in the exhausted gases. Despite the large use of this technique, the high operating temperature is still a limitation, promoting research of new SCR catalysts efficient at low temperature [2]. In this scenario, Manganese oxides-based catalysts have emerged in the last years for NOx-SCR because of their versatility, eco-compatibility and the presence of labile oxygen species. They showed excellent low-temperature performance in the SCR of NOx with ammonia (NH_3-SCR), both unsupported and loaded on different supports [3]. To enhance their catalytic activity, good dispersion, proper metal-support interaction and low metal loading are required.
In the present study, Mn/TiO_2 catalysts were prepared by one-pot reverse micelle sol-gel strategy (with the nominal metal content of 1, 5 and 10%). The reverse micelles approach provides an aqueous core that acts as a nanoreactor for the sol-gel templating of TiO_2 and simultaneously allows the dispersion of MnOx on the formed TiO_2 support. For comparison, a sample with a 10wt.% nominal Mn content was prepared by Incipient Wetness Impregnation (IWI) on mesoporous titania nanoparticles synthesized by the same reverse micelles procedure. The catalysts were characterized by using an integrated multi-techniques approach (XRD, H_2-TPR and NH_3-TPD, N_2 physisorption, FESEM and XPS).
The obtained results prove that the reverse micelle sol-gel approach allowed enhancing the catalytic activity, in that the catalysts were active in a broad temperature range at a substantially low Mn loading, as compared to the impregnated catalyst. Particularly, the 5 wt. % Mn catalyst showed the best NH_3-SCR activity in terms of both NOx conversion (ca. 90%) and amount of produced N_2O (ca. 50 ppm) in the 200-250 °C temperature range. This behaviour was assigned to the type of surface Mn species obtained by the reverse micelle sol-gel synthesis, favouring the formation of reduced Mn species (+2, +3) at the catalysts surface, strongly stabilized by the interaction with the support.

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Keywords
Selective Catalytic Reduction; Manganese oxide; Low-temperature activity; Reverse micelles.

Epoxidation of linseed oil by performic acid produced in situ: a kinetic study

Riccardo Tesser[a], Rosa Turco[a,b], Vincenzo Russo [a], Martino Di Serio[a], Elio Santacesaria[c],

[a] Department of Chemical Sciences, University of Naples Federico II, Complesso Universitario di Monte Sant'Angelo, Naples, Italy; [b] Institute for Polymers, Composites and Biomaterials, National Council of Research, Pozzuoli, Italy; [c] CEO of Eurochem Engineering LtD, Milano Italy;

The epoxidation of vegetable oils (VOs) gives place to products that are widely employed as plasticizers and stabilizers for PVC resins in substitution of phthalates that were banned in many countries for their negative effect on the health. Moreover, considering the high reactivity of the epoxy groups, the epoxidized vegetable oils are also useful as starting raw materials to produce a variety of chemicals such as polyols. For these reasons their production has shown in the recent years a significant growth in the world. Soybean Oil epoxidation is currently performed in semi-batch reactors using peracids (performic or peracetic) as oxidant species. For safety reasons the peracids are generated in situ by oxidation of an organic acid, such as formic or acetic acid, with hydrogen peroxide in the presence of a mineral acid (sulfuric or phosphoric) promoting the reaction as catalyst. The epoxidation process is quite complex involving several reactions, some occurring in the aqueous phase, others in the organic phase or at the water-oil interphase: (1) The oxidation of formic to performic acid, occurring in aqueous phase; (2) the epoxidation reaction, occurring in oil phase; (3) the ring opening reaction; (4) the performic acid decomposition, occurring in aqueous phase. Moreover, the epoxidation reaction is highly exothermic being ΔH= -55000 cal/mol for each reacted double bond, and efficient thermal control is needed in the industrial reactors to avoid runaway problems. For this reason, in the case of soybean oil, the reaction requires 8-10 hours to be completed, keeping the temperature between 60 and 70°C. Initially, the reaction is very fast and gives place to a steep rise of the temperature, then the reaction becomes slower, and the epoxide groups are subjected to the ring opening side reactions. Different papers, appeared in literature, dealing with the kinetics of the epoxidation of vegetable oil, applying an oversimplified pseudo-monophasic kinetic model to describe the complex process of the epoxidations and all the occurring reactions. Few biphasic kinetic models, reported in the literature, considered all the occurring mentioned reactions and the physical phenomena such as: (i) mass and heat transfer of the reagents between the two immiscible phases; (ii) solubilities of formic and performic acids in the oil phase; (iii) partition equilibria of formic and performic acids in the two phases. In order to individuate so many chemical and physical parameters it is opportune, when possible, to make independent experiments with the scope to reduce the parameters correlation. At this purpose, in our recent paper, a new biphasic model has been proposed to describe the epoxidation of soybean oil within situ formed performic acid, promoted by phosphoric acid as catalyst. In this work, we employed the same kinetic model for interpreting a set of epoxidation kinetic runs performed on linseed oil. Linseed oil has the peculiarity of a high unsaturation due to its composition rich of linolenic acid. In this study, we have found that linseed oil has a reactivity, in epoxidation reaction, 1.5 times higher than soybean oil, probably as a consequence of the great concentration of linolenic acid in the oil molecular structure. However, this enaced reactivty was observed also for the epoxidized prodyìucts, resulting ina reduction of selectivity. This well explain why the epoxidation of linseed oil must be conducted at temperatures lower than soybean oil to avoid as much as possible the occurrence ring opening undesired side reactions.

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Biochar and activated carbons from free-metals leather solid waste: characterization and engineering

Sebastiano Tieuli[a], Michela Signoretto[a], Riccardo Pasquale[b], Massimiliano Silvestri[c], Luca Frighetto[c]

[a]CATMAT Lab, Department of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and INSTM RU of Venice, via Torino 155, I-30172 Venezia, Mestre, Italy; [b]GSC GROUP S.P.A., Via dell'industria, 5, 36054 Montebello Vic.no, Vicenza Italy; [c]Pasubio S.p.A., II Strada 38, 36071 Arzignano, Vicenza Italy

Solid waste generated by the municipal and industrial sectors is a major problem worldwide due to issues associated with collection, transportation, treatment, and disposal [1]. The recycling and re-use of solid waste represent a great opportunity in terms of resource-saving, environmental protection and economic development. Leather manufacturing is classified as water, energy, and waste intensive and it is considered an activity demanding for integrated prevention and control of pollution. Along the whole process from raw hides to finished leather, a huge amount of solid and water waste is generated. One of the most abundant solid wastes (ca. 25% in weight of leather) is the shaving waste which results from the mechanical process that aims at reducing the tanned skin to a specific thickness [2].

The ongoing work proposes the optimization of an effective pyrolysis approach to convert metals-free leather shaving waste (by GOAST technology) into biochar and its subsequent physical activation process to design activated carbons [3]. Firstly, this study discusses the effect of pyrolysis parameters, such as temperature, residence time, heating, and inert flow rate on the biochar production.

Secondly, the attention was focused on the feasibility of using a physical activation process to engineering activated carbon starting from the biochar previously obtained. Therefore, the obtained materials were characterized by CHNS analysis, N_2 physisorption, FTIR, and XRD.

This study demonstrates as leather-shaving waste is a suitable carbonaceous precursor for the production of activated carbon. Furthermore, by defining the treatment parameters and selecting the activation agent, it is possible to modulate the morphological and chemical properties of the resulting activated carbon. This aspect provides useful information for the design of carbon materials that have the right characteristic according to the required application, such as catalysis, anodes for batteries, or supercapacitor.

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Heterogeneous photodegradation for abatement of recalcitrant COD in the wastewater derived from the tanning industry.

M.Toscanesi [a], M. Di Serio [a], A. Giarra [a], V. Russo [a], M. Trifuoggi [a].*

[a] *Department of Chemical Sciences, University of Naples Federico II, Via Cintia – 80126, Naples, Italy.*
**correspondence: maria.toscanesi@unina.it*

The wastewater from the tanning industry is a serious environmental problem, as it has high concentrations of organic and inorganic contaminants. In the tannage operation, the skin is treated with various chemicals such as chromium salts, vegetable substances, aldehydes, oils, etc. Subsequently they undergo retanning and finishing processes to give the leather the desired characteristics for marketing.

In the various stages of tanning many compounds are used such as acids, alkalis, chromium salts, tannins, solvents, dyes, oils, resins, synthetic tannins, but they aren't completely fixed on the skin and remain in the water. Then high values of chemical oxygen demand (COD), biochemical oxygen demand (BOD), sulphate, chloride, heavy metals and various organic substances characterize the discharged wastewaters. COD is one of the main parameters used to evaluate the quality of wastewaters; in particular, it is able to provide indications on the content of organic matter. We can distinguish two fractions for the COD: the biodegradable one, represented by all those compounds that are removed from urban or industrial wastewater through traditional purification processes, and the not-biodegradable fraction, represented by all those substances defined as "recalcitrant" and which they persist after the common treatments [1].

The increase of these compounds in wastewaters and the concern about the unknown long-term effects of their accumulation in the environment brought researchers to a growing awareness about the need to improve existing technologies and to develop new strategies for the removal of this new class of pollutants from wastewater [2].

Over the years, adsorption and photodegradation were proved to be efficient methods for wastewater treatment due to their high efficiency and low costs, also thanks to the employment of solid materials which can be easily separated and reused [3,4]: for this reason, these technologies are promising for the removal of organic contaminants from waters. The aim of this work is to conduct an in-depth study of the recalcitrant COD abatement processes, using heterogeneous photodegradation, catalysed by inorganic nanocrystalline semiconductor (commercial TiO_2), to maximize the efficiency of these methods.

The photodegradation experiments will take place in a 1.5 L glass-lined reactor, thermostated and magnetically stirred, in which the air will be bubbled through a mesh filter. The irradiation will be provided through a UV lamp (365nm) inserted coaxially into the reactor.

As revealed, an increase of the decomposition rate is observed when increasing the initial pollutant concentration.Further elaboration will lead us to the determination of kinetic parameters for the mentioned processes.

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Cynara cardunculus: an example of zero waste biorefinery for biomass exploitation

R. Turco[a,b], I. Corrado[a], M. Malinconico[b], C. Pezzella[c], G. Sannia[a], G. Santagata[b], R. Tesser[a], D. Zannini[b], M. Di Serio[a]

[a] Department of Chemical Sciences, University of Naples Federico II, Complesso Universitario di Monte Sant'Angelo, Naples, Italy; [b] Institute for Polymers, Composites and Biomaterials, National Council of Research, Pozzuoli, Italy; [c] Department of Agricultural Sciences, University of Naples Federico II, Portici, Italy

Cardoon, *Cynara cardunculus* L. from Asteraceae family, represents a challenging, strong, non-food chain competitive crop, able to grow in dry, marginal lands and/or polluted soils of many Mediterranean regions, already exploited for industrial pulp and paper production and domestic heating.
The recently founded national Italian project "CARDIGAN" aims at exploiting a "Cardoon biorefinery model" by a holistic approach. The idea is to valorize all fractions derived by cardoon to obtain high added value products. In this scenario CARDIGAN project aims to design bioplastics from Cardoon, by biological and chemical transformation of its different fractions, such as roots and seeds.
Poly(3-hydroxybutyrate) (PHB) is a homopolymer of 3-hydroxybutyrate, the most significant member of the biodegradable thermoplastic polyhydroxyalkanoates (PHA) family, showing physical properties comparable to those of some petroleum-based polymers. Despite this, PHB use is hampered by its narrow temperature range of processability and by its high crystallinity. Use of plasticizers could solve this issue by reducing brittleness and improving processability [1].
In this work, PHB has been obtained by a simultaneous Saccharification and Fermentation (SSF) of inulin derived from cardoon roots [2]. To improve the properties, two type of additives have been Furthermore, oil extracted from cardoon seeds, has been tested as C-source for the production of medium-chain length PHA (mcl-PHA) and has been chemically epoxidized to be used as green and non-toxic biodegradable PHB plasticizers, preserving the eco-sustainability of the whole system.
Aimed at widening the industrial applicability of PHB, the synthesised PHB polymer, epoxidized oil and mcl-PHA have been formulated in blends to develop PHB based films with optimized, chemical-physical and mechanical properties [3]. The cardoon biomass recovery, separations into different components and their following recombination in upgraded materials can be framed in a holistic approach of zero waste circular economy.

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The Impact of Charge in a Ni(II) Polymerization Catalysts

Maria Voccia,[a] Eva Schiebel,[b] Laura Falivene,[a] Stefan Mecking,[b] Lucia Caporaso[a]*

[a] Department of Chemistry, University of Salerno (Italy); [b]Department of Chemistry, University of Konstanz (Germany)

Among the late transition metal catalysts active in the ethylene polymerization, an interesting class of compounds is represented by Ni (II) salicylaldiminato complexes [1,2,]. Recently, a second imine donor was introduced in the form of bis(imino)-phenoxy motifs. These complexes proved to be promising candidates for obtained products whose microstructure is strictly dependent on the catalyst structure, moving from high-molecular-weight polyethylene to oligomers (1).
A direct comparison between neutral active catalysts (Chart 1) and their corresponding cationic analogues (Chart 2) is enabled by protonation of neutral bis(imino)phenoxy complexes. For the neutral species compared to the highly studied mono(imino)-phenoxy complexes (2, 3), the second imine motif does not influence the microstructure of the polymerization' products, being directed away from the active site. But it allows for the incorporation of a proton in proximity of the active center in an N···H+···O bridge yielding the protonated species. The bridge weakens the Ni−O bond and decreases the electron density at the metal.
Experimentally, the two catalysts which in their neutral version produce linear HDPE or undergo extensive chain walking, if cationically charged always produce short chain oligomers.

A mechanistic analysis by DFT methods reveals an increased propensity for β-hydride elimination compared to ethylene insertion chain growth for the cationic complexes. This results from a higher relative stability of β-agostic species vs olefin-coordinated species.

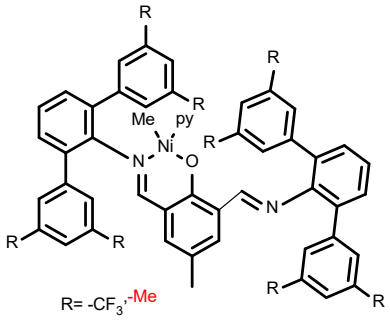

Chart 1

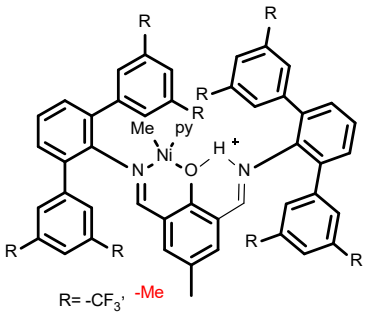

Chart 2

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Development and engineering of hybrid systems based on inorganic nanoparticles and microalgae to be applied in wastewater remediation

Andrea Brigliadori[a,b], Magda Blosi[b], Ilaria Zanoni[b], Stefania Albonetti[a,b]

[a] Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale Risorgimento 4, Bologna (BO), 40136, Italy; [b] ISTEC-CNR, Institute of Science and Technology for Ceramics, National Research Council, Via Granarolo 64, Faenza (RA), 48018, Italy.

This work aims to produce and engineer new hybrid systems obtained by coupling titania nanoparticles with *Chlorella Vulgaris* microalgae for application in wastewater treatment. The study was aimed at optimizing the material, which integrates two properties: the photocatalytic activity exploited for the degradation of organic pollutants, conferred by TiO_2 coupled with SiO_2[1], and the biosorption of the heavy metal, typical of the biomass[2]. The results showed positive synergistic effects promoted by the microalgae dispersion on the oxide surface so enhancing the bioremediation performance of the material. In order to foster the industrial application of the prepared catalytic system, the suspensions were engineered by removing the solvent by a Spray-Freeze-Drying technology[3]. Moreover, a wide-ranging characterization was carried out both on suspensions (ELS, DLS) and on dried granules (BET, SEM-FEG, SEM-EDS) to optimize the formulation and correlate the physicochemical properties with the functional performances. The functional properties were evaluated by using as probe reaction the photodegradation of Rhodamine B and by assessing the absorption of copper ions.

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Direct synthesis of hydrogen peroxide: role of catalytic support and selectivity enhancers on long-term catalytic tests

Francesco Sandri[a], Lorenzo Franco[a], Marco Zecca[a], Paolo Centomo[a]

[a] *Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1-I35131 Padova (Italy)*

The Thesis project is focused on nanostructured palladium catalysts for the direct synthesis (DS) of hydrogen peroxide (HP).[1] Specifically, the aim of this project is the detailed investigation of important features of the reaction typically reported on literature, but still not rationalized, such as the role of the catalytic support and selectivity promoters.[2] The effect of the morphology of the catalytic support for the DS is evaluated, demonstrating that mesoporous supports show higher HP selectivity, making more efficient the back-diffusion of the desired product towards the bulk solution.[3] Moreover, the catalytic system has been investigated in long time tests (50 hours instead the 2-4 hours typically reported in literature). It appears that, under semi-batch conditions, the catalytic activity remains constant for indefinite times, but with a high selectivity towards HP only during the first 2 hours of reaction; this makes unpromising the exploitation of such a catalytic system for technological applications. However, catalysts based on mesoporous resins are extremely selective during the firsts hours of reaction, suggesting the development of continuous catalytic systems, based on a fixed-bed reactor, always operating under the highest selectivity conditions. In addition, the effect of supported acid groups and the halides as selectivity enhancers has been investigated. To this regard, the degradation phenomenon on the catalyst and the reactor, during 24-hour tests have been studied. By operating under very high concentration of bromide ions (120 ppm) for very long reaction times, several unexpected behaviors of the catalyst have been observed. In fact, it seems necessary to take into the account also the redox behavior of the halide ions to better define their role in the DS. Finally, some catalysts, recovered after the DS reaction, have been characterized with SEM, EDX and EPR, to determine the main chemical modifications. This allowed to evaluate the possible role of the polymer supports, in an oxidative environment, in the formation of peroxide species in solution. In fact, it is clearly observed that ion exchange resins undergo to auto-oxidation phenomena, under mild conditions, with the consequent formation and release of HP. An important aspect that must be clarified in further investigations is the mechanism leading to the formation of peroxide species, to define the possible role of the polymer support as redox mediator in the formation of HP.

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Design of non-conventional chemical processes for biomass valorization

Giorgio Grillo,[a] Silvia Tabasso,[b] Maela Manzoli,[a] Emanuela Calcio Gaudino,[a] Francesco Mariatti,[a] Fabio Bucciol,[a] Giancarlo Cravotto[a]

[a] Department of Drug Science and Technology, University of Turin, Via P. Giuria 9, 10235 Turin, Italy;
[b] Department of Chemistry, University of Turin, Via P. Giuria 7, 10125, Turin, Italy.

Despite chemical industry still runs mainly with fossil feedstock, the demand for renewable sources has steadily increased over the last two decades. In this frame, biomass and bio-wastes have been recognized as renewable source of fixed carbon for the production of valuable platform chemicals for industrial applications. In the meantime, new enabling technologies for processes intensification have been developed and successfully applied in this field. Microwaves (MW), ultrasound (US), hydrodynamic cavitation (HC) may generate high-energy microenvironments. The aim of this work was the design of new processes based on non-conventional technologies for biomass extraction and selective conversion. The investigation started on batch reactors provided suitable data for systems scale up, towards industrial applications. Furthermore, the target is a zero-wastes protocol to treat different biomasses following a circular economy approach. The combination of new green solvents, sustainable heterogeneous catalysts and non-conventional chemical reactors opened new paths for biomass conversion. Well-balanced cascade process enabled a full valorization of biomass constituents and by-products into high-value-added chemicals. According to this strategy, four pivotal steps have been deeply investigated: (I) Metabolites Extraction, (II) Pre-treatment, (III) Structural Conversion and (IV) Platform Modification.

Extractions (I) can provide several valuable secondary metabolites, such as polyphenolic compounds. Different protocols have been optimized, by kinetic studies, among vegetal residual matrixes: cocoa shells, curcuma, tea, grape stalks and pomace. Structural biopolymers, as alginates from algae, pectins from citrus wastes, and lignin from lignocellulosic materials could be isolated within the same protocols. Green solvents play a key role for new and sustainable pre-treatment (II), showing surprising synergies with non-conventional techniques to achieve fractions enriched in lignin-derived polyphenols and solid residues suitable for the conversion into fermentable sugars, after enzymatic hydrolysis. Enabling technologies exhibit synergistic effects also with heterogeneous catalysts, mainly due to hot-spots generation on the active sites. This feature can be applied for structural biopolymers conversion (III) into valuable building blocks: hydrolysis and isomerization have been exploited to produce monosaccharides, hydroxymethylfurfural (HMF) or levulinic acid from cellulose and hemicellulose. For these purposes, solid acid catalysts as sulfated zirconia and zeolites have been studied. A further modification of biobased derivatives could be carried out via reduction reactions under heterogeneous catalysis with Au, Pd or Ru nanoparticles supported on TiO_2, ZrO_2, Al_2O_3 or AC. The main products obtained were γ-valerolactone (GVL) and 1,4-pentanediol. The best performing protocols of the cascade process have been chosen for the scaling up, increasing batch volumes towards pilot scales (75L), or moving to flow systems, with pre-industrial flow-rates (from 1L/h to 20L/min). Final tests were carried out in a plant working with 50 kg/die of lignocellulosic residues to obtain fermentables, boosting the delignification percentage of the matrix. On the other hand, the biomass delignification was also achieved through an integrated process: biowastes were treated in GVL to recover pure lignin and to convert cellulose into levulinic acid, which was then hydrogenated to GVL. Following a circular approach, the solvent was regenerated and recycled for next delignification steps.

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INDICE COMUNICAZIONI ORALI

Astolfi	Paola	TEC OR042
Atzori	Matteo	INO OR025
Audisio	Davide	ORG OR003
Avola	Tiziana	ANA OR086
Ayaz	Nazeeha	TEC OR027
Aye	Yimon	FAR KN005
Bacchiocchi	Riccardo	IND OR058
Baccolo	Giacomo	ANA OR034
Bach	Anders	FAR KN009
Badetti	Elena	ABC OR007
Baglio	Vincenzo	ELE OR57
Baglioni	Michele	FIS OR076
Baldassarre	Francesca	TEC OR041
Baldelli	Francesca	FIS OR067
Baldini	Laura	ORG OR087
Ballarotto	Marco	ORG OR019
Balliana	Eleonora	ABC OR002
Balsamo	Stefano Andrea	IND OR047
Bandiera	Tiziano	FAR KN011
Baratta	Mariafrancesca	FIS OR107
Barbanente	Alessandra	INO PZ008
Barbera	Vincenzina	TEC OR021
Barberis	Elettra	MAS OR005
Barbieri	Luisa	ABC OR054
Barbieri	Pierluigi	ABC OR058
Bardi	Brunella	FIS OR103
Barlocco	Ilaria	INO OR002
Barola	Carolina	MAS OR011
Baron	Marco	INO OR019
Barone	Laura	ANA OR114
Barreca	Marilia	FAR OR011
Bartella	Lucia	MAS OR010
Battista	Sara	ORG OR004
Battistuzzi	Gianantonio	CSB OR003
Begni	Federico	FIS OR088
Bella	Federico	IND OR036
Bellassai	Noemi	ANA OR068
Bellavita	Rosa	FAR OR042
Bellia	Francesco	CSB OR022
Bellina	Fabio	ORG OR069
Bellini	Marco	INO OR041
Belloni	Alessia	INO OR048
Bellotti	Denise	ANA OR087
Bellotto	Ottavia	CSB OR002
Benedetti	Michele	INO OR008
Bernardi	Anna	ORG PZ001
Bernes	Elisa	TEO OR017
Bernini	Roberta	ORG OR005
Bertani	Marco	TEO OR001
Bertinetti	Stefano	ANA OR060
Berto	Silvia	ANA KN010

Bertucci	Alessandro	ANA OR069
Bertuletti	Susanna	ORG OR117
Bertuzzi	Giulio	ORG OR108
Bettini	Simona	FIS OR080
Biagini	Denise	ANA OR035
Biagiotti	Giacomo	ORG OR027
Bianchera	Annalisa	TFA OR010
Bianchi	Federica	ANA OR076
Bianco Prevot	Alessandra	ANA IL005
Biancolillo	Alessandra	ANA KN004
Biasi	Pierdomenico	IND KN003
Biesuz	Raffaela	ANA OR123
Biffis	Andrea	INO OR022
Bifulco	Aurelio	TEC OR017
Biggio	Deborah	ANA OR115
Bigogno	Alessandra	ABC OR006
Bisag	Denisa	ORG OR118
Biscaglia	Francesca	FIS OR064
Bizzarri	Bruno Mattia	ORG OR020
Blangetti	Nicola	FIS OR111
Blasi	Davide	ORG OR028
Bloise	Ermelinda	TEC OR004
Bogialli	Sara	MAS KN003
Boldrini	Chiara Liliana	ORG OR080
Bollella	Paolo	ANA KN009
Bolognesi	Margherita	FIS OR049
Bonacchi	Sara	ELE OR11
Bonaccorso	Angela	TFA OR002
Bonfio	Claudia	CSB PZ002
Bonini	Andrea	ANA OR017
Bonini	Mauro	TFA IL003
Bonizzoni	Simone	ELE OR53
Bonomo	Matteo	ELE KN34
Bonomo	Matteo	IND OR039
Borella	Matteo	IND OR064
Bortolato	Tommaso	ORG OR109
Bossi	Alberto	ORG OR029
Bossi	Alessandra Maria	ANA OR070
Botla	Vinayak.	IND OR010
Braconi	Laura	FAR OR012
Branchini	Federica	DID OR001
Brandi	Jessica	ANA OR095
Brandiele	Riccardo	ELE IL31
Bretti	Clemente	ANA KN002
Brilloni	Alessandro	ELE OR67
Brufani	Giulia	ORG OR119
Brugnoli	Luca	TEO OR006
Brunelli	Andrea	ABC OR015
Brunetti	Leonardo	FAR OR009
Brunsveld	Luc	CSB KN003
Budroni	Marcello	FIS OR122

Buonsenso	Fabio	ORG OR033
Busato	Matteo	FIS OR094
Buscemi	Gabriella	ORG OR081
Cabri	Walter	IND KN002
Cademartori	Davide	ELE OR56
Caflisch	Amedeo	CSB KN006
Calà	Elisa	ANA OR063
Calabrese	Carla	IND OR024
Calandra	Pietro	ABC OR055
Calandra	Pietro	FIS OR085
Calcaterra	Andrea	ORG OR006
Calcio Gaudino	Emanuela	ORG OR120
Calgaro	Loris	ABC OR056
Calogero	Francesco	ORG OR121
Calvano	Cosima Damiana	ANA IL004
Calvini	Rosalba	ANA OR132
Calvino	Martina Maria	FIS OR118
Campagnolo	Filippo	INO OR024
Campanella	Beatrice	ANA OR116
Campiani	Giuseppe	FAR KN001
Campisciano	Vincenzo	ORG OR122
Campisi	Sebastiano	FIS OR034
Campisi	Sebastiano	IND OR014
Campitelli	Patrizio	INO OR037
Cannavacciuolo	Ciro	MAS OR009
Capone	Matteo	TEO OR015
Cappai	Rosita	ANA OR088
Caprioglio	Diego	ORG OR021
Capriotti	Anna Laura	ANA IL009
Caputo	Paolino	FIS OR040
Cara	Claudio	FIS OR105
Caratelli	Veronica	ANA OR134
Carbone	Daniela	FAR OR013
Cardoso Gomes	Guelber	TEO OR016
Carena	Luca	ANA OR061
Carmignani	Alessio	FIS OR099
Carpanese	Maria Paola	ELE OR48
Carpentieri	Maria Antonietta	DID OR002
Carucci	Cristina	FIS OR063
Caruso	Manfredi	TEC OR005
Casini	Angela	CSB KN005
Castiglione	Franca	TEC OR010
Casula	Luca	TFA OR011
Cataldo	Salvatore	ANA OR089
Catani	Martina	ANA PZ004
Catelli	Emilio	ANA OR064
Catto	Marco	FAR OR031
Cavalera	Simone	ANA OR096
Cavazza	Antonella	ANA OR025
Cavuoto	Denise	IND OR002
Cecchi	Teresa	DID OR010

Cecconi	Daniela	MAS OR001
Ceccucci	Anita	TEC OR045
Cefali	Manuel Amedeo	ABC OR059
Centomo	Paolo	INO OR033
Cerrato	Andrea	ANA OR097
Cerri	Luca	TFA OR012
Cesari	Cristiana	INO OR035
Chelazzi	David	FIS OR 129
Chenet	Tatiana	ANA OR026
Chiarcos	Riccardo	IND OR027
Chiarello	GianLuca	FIS OR030
Chino	Marco	INO OR032
Chiodo	Fabrizio	ORG OR007
Chirizzi	Cristina	FIS OR081
Ciacci	Luca	ABC OR003
Ciccola	Alessandro	ABC OR008
Cinti	Stefano	ANA OR071
Cioffi	Nicola	ANA IL010
Cipriano	Domenico	ABC OR045
Cirillo	Martina	ORG OR008
Clemente	Ilaria	FIS OR065
Cleto Bruzzese	Paolo	INO OR027
Colella	Marco	ORG OR022
Colella	Maria Francesca	FIS OR115
Collini	Elisabetta	FIS OR047
Colloca	Stefano	TFA IL002
Colozza	Noemi	ANA OR135
Comis	Silvia	ELE OR43
Condorelli	Marcello	FIS OR009
Consentino	Luca	IND OR015
Conte	Francesco	IND OR045
Contente	Martina	FAR OR018
Conti	Luca	INO OR023
Coralli	Irene	ANA OR077
Corbisiero	Dario	ORG OR023
Cordaro	Massimiliano	ORG OR024
Corinti	Davide	INO OR063
Corno	Marta	FIS OR101
Corradini	Danilo	ANA OR024
Corrente	Giuseppina Anna	FIS OR035
Corrieri	Matteo	ORG OR132
Cosentino	Ugo	DID OR015
Costa	Maria	DID OR003
Costanzo	Paola	ORG OR061
Cozzolino	Antonietta	IND OR028
Cristiano	Maria Chiara	TFA OR013
Cristina	Tealdi	ELE KN68
Crivellaro	Giovanni	ELE OR07
Crocetti	Letizia	FAR OR006
Cucinotta	Lorenzo	ANA OR003
Cupellini	Lorenzo	TEO PZ005

Curti	Claudio	ORG OR059
D'Ambrosio	Valeria	ABC OR022
D'Imperio	Nicolas	ORG PZ012
Da Pian	Marta	ORG OR034
D'Agata	Roberta	ANA OR117
Dai	Yasi	TEO OR018
Dal Bello	Federica	ANA OR028
Dall'Anese	Anna	INO PZ002
D'Alterio	Massimo Christian	INO OR004
D'Amato	Alfonsina	ANA OR105
Damiano	Caterina	INO OR016
Damin	Alessandro	FIS OR126
Danielis	Maila	IND OR005
D'Aria	Federica	FIS OR018
Darjazi	Hamideh	ELE OR72
Davighi	Maria Giulia	ORG OR010
de Araujo Lima e Souza	Giselle	TEC OR011
De Bon	Francesco	ELE OR16
De Bonis	Angela	FIS OR097
De Castro	Cristina	ORG OR011
De Ceglie	Cristina	ABC OR017
De Filpo	Giovanni	FIS OR082
De Gennaro	Gianluigi	ABC OR001
De Grazia	Gemma	ANA OR004
De Leo	Vincenzo	FIS OR019
De Luca	Chiara	ANA OR106
De Marchi	Fabiola	MAS OR008
De Santis	Roberto	FIS KN012
De Santis	Serena	TEC KN003
De Zotti	Marta	CSB OR001
Deganello	Francesca	INO OR039
Degli Esposti	Lorenzo	FIS OR021
Del Coco	Laura	INO OR061
Del Galdo	Sara	TEO OR022
Del Giudice	Alessandra	FIS OR053
Del Giudice	Daniele	ORG OR088
Del Grosso	Erica	ANA OR072
Della Pelle	Flavio	ANA KN011
Dell'Edera	Massimo	FIS OR113
Deng	Siyuan	TFA OR009
Desantis	Jenny	ORG OR012
Dettin	Monica	FIS OR096
Di Capua	Angela	ANA OR098
Di Carlo	Gabriella	FIS KN010
Di Carluccio	Cristina	ORG OR013
Di Carmine	Graziano	ORG OR035
Di Donato	Francesca	ANA OR036
Di Fidio	Nicola	IND OR053
Di Giulio	Tiziano	ANA OR018
Di Guida	Rossella	ORG OR014
Di Liberto	Giovanni	FIS OR028

Di Liberto	Giovanni	TEO PZ003
Di Maiolo	Francesco	TEO OR029
Di Maro	Mattia	ORG OR110
Di Maro	Salvatore	FAR OR039
Di Matteo	Paola	TEC OR025
Di Muzio	Simone	FIS OR071
Di Nardo	Fabio	ANA OR099
Di Noja	Simone	ORG OR031
Di Pietro	Maria Enrica	TEC OR012
Di Porzio	Anna	CSB OR029
Di Terlizzi	Lorenzo	ORG OR063
Dibenedetto	Carlo Nazzareno	FIS OR001
Dichiara	Maria	FAR OR021
Dichiarante	Valentina	TEC OR031
Dilonardo	Elena	TEC OR028
Dini	Danilo	ELE OR17
Dispenza	Clelia	TEC OR046
Distefano	Alessia	CSB OR009
Dogra	Raghav	ANA OR009
Domestici	Chiara	INO OR042
Donà	Lorenzo	TEO OR030
Donati	Greta	TEO PZ001
Donato	Paola Agata	ANA OR030
Donnarumma	Danilo	ANA OR118
Donnoli	Maria Irene	DID OR011
D'Onofrio	Mariapina	ORG OR009
Dozzi	Maria Vittoria	FIS KN009
D'Urso	Alessandro	CSB OR010
Econdi	Stefano	IND OR011
El Fadil	Dounia	ANA OR107
Elbaz	Lior	ELE KN55
Elkhanoufi	Sabrina	CSB OR008
Elliani	Rosangela	ANA OR005
Erba	Alessandro	TEO PZ002
Ermini	Elena	ORG OR036
Escolano Casado	Guillermo	FIS OR069
Esposito	Anna	ORG PZ014
Esposito	Germana	ORG OR037
Esposito	Roberto	INO OR020
Esposito	Rodolfo	FIS OR106
Esposito	Tiziana	TFA OR014
Espro	Claudia	TEC KN001
Estima Gomes	Manuela	TFA IL005
Fabbiani	Marco	FIS OR006
fabbri	Debora	ANA OR029
Fabiani	Laura	ANA OR019
Facchetti	Giorgio	INO OR031
Facchin	Alessandro	ELE OR35
Facchin	Alessandro	ELE OR51
Faginas-Lago	Noelia	TEO OR008
Fagiolari	Lucia	IND OR061

Fagnani	Francesco	INO OR007
Falco	Marisa	ELE OR62
Falletta	Ermelinda	IND OR048
Famulari	Antonino	INO OR062
Fanizza	Elisabetta	FIS OR014
Fanti	Federico	MAS OR004
Fasano	Valerio	ORG OR116
Fasolini	Andrea	IND OR040
Fasulo	Francesca	TEO OR009
Fattal	Elias	TFA IL001
Federico	Bella	TEC OR038
Felletti	Simona	ANA OR078
Fenti	Angelo	ABC OR009
Ferdeghini	Claudio	ORG OR032
Ferdinando Summa	Francesco	TEO OR023
Ferlenghi	Francesca	FAR OR019
Fermi	Andrea	INO OR045
Fermo	Paola	ANA IL006
Feroci	Marta	ELE KN045
Ferracane	Antonio	ANA OR006
Ferrari	Giorgio	IND OR065
Ferraro	Giovanni	FIS OR011
Ferrauto	Giuseppe	INO OR051
Ferrazzano	Lucia	ORG OR064
Ferrero	Luca	ABC OR005
Ferretti	Francesco	INO OR021
Fidaleo	Marco	TFA IL004
Filippin	Ilaria	TFA OR003
Fiorentini	Carlo	DID IL002
Fiorentino	Antonino	ABC OR034
Fiorenza	Roberto	IND OR016
Fiorito	Daniele	ORG OR060
Fischer	Peter	ELE KN06
Forchetta	Mattia	ORG OR082
Fornari	Fabio	ANA OR037
Fornasier	Marco	FIS OR016
Forni	Alessandra	FIS OR044
Fortino	Mariagrazia	TEO OR010
Fortunati	Alessia	ELE OR21
Foschi	Francesca	ORG OR123
Francesconi	Oscar	ORG OR089
Franchina	Flavio	ANA KN001
Franchino	Allegra	ORG OR067
Franco	Francesca	ORG OR076
Franzini	Roberta	ORG OR038
Frateloreto	Federico	ORG OR133
Freccero	Riccardo	INO OR069
Frosi	Ilaria	FAR OR017
Froudakis	George	FIS KN007
Funicello	Maria	ORG OR015
Gabas	Fabio	FIS OR058

Gaeta	Massimiliano	CSB OR021
Gaggero	Elisa	ABC OR035
Gaggiotti	Sara	ANA OR124
Gagliardi	Anna	IND OR049
Galantini	Luciano	FIS KN011
Galassi	Rossana	INO OR047
Galeotti	Marco	ORG OR039
Galletta	Micaela	ANA OR007
Galloni	Melissa Greta	IND OR017
Gambassi	Francesca	INO OR049
Garbarino	Gabriella	IND OR006
García Lascurain	P. Guzmán	ABC OR046
Garello	Francesca	INO OR054
Gaspa	Silvia	ORG OR070
Gatti	Lucrezia	ABC OR028
Gatto	Emanuela	FIS KN003
Gazzola	Silvia	ORG OR138
Gazzotti	Stefano	IND OR023
Gelain	Arianna	FAR OR014
Gelli	Rita	FIS OR052
Geninatti	Simonetta	INO OR084
Gentile	Luigi	FIS KN004
Gentili	Dario	ORG OR016
Gentili	Pier Luigi	FIS OR038
Gessner	Viktoria	INO IL001
Ghedini	Elena	IND OR070
Ghini	Veronica	CSB OR006
Ghini	Veronica	INO OR070
Ghirga	Francesca	ORG OR041
Giacalone	Francesco	ORG PZ007
Giambastiani	Giuliano	IND OR063
Giannetto	Marco	ANA OR073
Giedroc	David	INO IL003
Gilda Ritacca	Alessandra	TEO OR020
Gioiello	Antimo	FAR KN006
Giordana	Alessia	INO OR030
Giorgi	Silvia	IND OR057
Giorno	Lidietta	CSB OR004
Giovanni	Falcone	TEC OR044
Giovannini	Tommaso	FIS OR060
Girlando	Alberto	FIS OR090
Girolametti	Federico	ANA OR010
Giuffrè	Ottavia	ANA OR090
Giuliano	Elena	TFA OR017
Giurlani	Walter	ANA OR119
Giustiniano	Mariateresa	FAR PZ002
Gobbo	Pierangelo	ORG PZ004
Gobetto	Roberto	INO OR001
Gois	Pedro	FAR KN012
Golla	Manohar	IND OR029
Goracci	Laura	ORG OR042

Gori	Alessandro	TEC IL003
Gorla	Giulia	ANA OR120
Goti	Giulio	ORG OR083
Grattieri	Matteo	ELE OR18
Grigioni	Ivan	IND OR035
Groppo	Elena	FIS KN005
Gualandi	Andrea	ORG OR134
Gualandi	Isacco	ANA KN007
Gubitosa	Jennifer	FIS OR024
Guerra	Giulia	ABC OR036
Gugliuzza	Annarosa	ABC OR043
Guidoni	Leonardo	TEO OR013
Guidotti	Giulia	ABC OR021
Guidotti	Matteo	IND OR067
Gullifa	Giuseppina	ANA OR079
Guzman	Hilmar	ELE OR23
Hajareh Haghighi	Farid	INO OR066
He	Xiufang	ELE OR39
Hernandez	Simelys	IND OR034
Hessel	Volker	IND KN007
Hirsch	Anna	FAR KN008
Hmoudah	Maryam	IND OR071
Iaccarino	Nunzia	CSB OR027
Iammarino	Marco	ANA OR031
Ianni	Federica	FAR OR016
Illiano	Anna	ANA OR008
Illuminati	Silvia	ANA OR062
Impemba	Salvatore	INO OR052
Imperatore	Concetta	ORG OR043
Inaudi	Paolo	ANA OR044
Intagliata	Sebastiano	FAR OR028
Interino	Nicolò	ANA OR100
Irto	Anna	ANA OR091
Jacobson	Kenneth	FAR MD001
Joseph	Edith	ABC KN001
Jurinovich	Sandro	DID OR004
Kaveh	Moulaee	TEC OR035
Keserű	György	FAR KN002
Khalid	Shahid	ELE OR75
Koper	Marc	ELE KN19
Kuhnert	Nikolai	MAS PL003
La Nasa	Jacopo	ANA OR080
La Regina	Giuseppe	FAR OR004
La Tella	Roberta	ANA OR081
Labarile	Rossella	FIS OR015
Labate	Maria	ABC OR025
Lacarbonara	Giampaolo	ELE OR08
Lambruschini	Chiara	ORG OR040
Lamuraglia	Raffaella	ABC OR029
Lancellotti	Isabella	TEC OR018
Larisa	Lvova	TEC IL002

Laudadio	Gabriele	ORG PZ015
Laurati	Marco	FIS KN001
Laus	Michele	IND KN004
Lazzara	Giuseppe	ABC OR050
Leccese	Mirko	FIS OR102
Lenci	Elena	DID OR012
Lenci	Elena	ORG PZ009
Lenzi	Alessio	ANA OR108
Leonardo	Duranti	ELE OR49
Leone	Linda	INO OR005
Leonelli	Cristina	TEC OR016
Lesch	Andreas	ANA OR045
Li	Min	ANA OR121
Liccardo	Letizia	INO OR055
Licen	Sabina	ABC OR010
Licen	Sabina	ANA OR038
LiDestri	Giovanni	FIS OR002
Lipparini	Filippo	TEO OR025
Lippi	Martina	TEC OR033
Lisuzzo	Lorenzo	FIS OR072
Litti	Lucio	FIS OR078
Lo Porto	Chiara	FIS OR108
Lo Vecchio	Carmelo	ELE OR03
Locatelli	Marcello	ANA OR082
Lodesani	Federica	TEO OR031
Lodi	Giulia	ABC OR032
Loianno	Valerio	FIS OR086
Lombardi	Dora Stella	DID OR005
Lombardo	Marco	ORG OR135
Lopreside	Antonia	ANA OR074
Losi	Niccolo	ABC OR060
Lovison	Denise	INO OR056
Lucantonio	Stefania	IND OR060
Lucarini	Marco	ORG PZ005
Lucarini	Simone	FAR OR024
Lucenti	Elena	INO OR014
Lufrano	Ernestino	ELE OR65
Lunardon	Marco	INO OR072
Lupi	Michela	ORG OR136
Lupidi	Gabriele	ORG OR145
Luque	Rafael	IND KN006
M. Fiore	Ambra	TEC OR019
Maccarone	Giuseppina	MAS PL001
Macchia	Eleonora	ANA OR020
Magnaghi	Lisa Rita	ANA OR039
Magni	Mirko	ELE OR26
Mai	Antonello	FAR MD002
Maiuolo	Loredana	ORG OR074
Malacaria	Luana	ANA OR092
Malegori	Cristina	ANA KN005
Malferrari	Marco	ELE OR37

Malitesta	Cosimino	ANA OR136
Mameli	Valentina	FIS OR010
Manca	Gabriele	INO OR057
Mancinelli	Michele	ORG OR075
Mancini	Alessandro	ABC OR061
Manfredi	Marcello	ANA OR109
Manfredi	Norberto	ORG OR084
Mangini	Anna	ELE OR66
Mangraviti	Domenica	ANA OR051
Mannias	Giada	INO OR075
Mantovani	Marco	ABC OR020
Manzoli	Maela	IND OR051
Marasco	Daniela	INO OR060
Marassi	Valentina	ANA OR101
Marchesi	Stefano	FIS OR110
Marchiò	Luciano	INO OR077
Marcì	Giuseppe	TEC OR029
Marcolin	Giampaolo	FIS OR043
Maresca	Giovanna	ELE OR74
Maria Squeo	Benedetta	ORG OR106
Mariani	Federica	ANA OR021
Mariconda	Annaluisa	INO OR068
Mariotti	Nicole	IND OR032
Marittimo	Nicole	ANA OR052
Marotta	Angela	TEC OR009
Martella	Daniele	IND OR031
Martelli	Giulia	ORG OR137
Martina	Bortolami	TEC OR040
Martini	Francesca	FIS OR048
Martí-Rujas	Javier	INO OR006
Maruccia	Elisa	ELE OR20
Marullo	Salvatore	ORG OR111
Marussi	Giovanna	ANA OR065
Marzo	Tiziano	INO OR011
Mascolo	Giuseppe	ABC OR037
Mascolo	Giuseppe	ABC OR038
Masi	Marco	ORG OR044
Massari	Serena	FAR OR036
Massaro	Arianna	TEO OR002
Massaro	Marina	ORG OR054
Mastrangelo	Rosangela	FIS OR074
Mattarozzi	Monica	ANA OR102
Maturi	Mirko	ORG PZ013
Mauriello	Francesco	IND OR059
Mauriello	Francesco	TEC OR002
Mazzapioda	Lucia	ELE OR52
Mazzaracchio	Vincenzo	ANA OR022
Mazzariol	Chiara	INO OR080
Mazzei	Luca	CSB PZ001
Mazzoni	Rita	INO OR043
Mazzucato	Marco	ELE OR12

McLean	John	MAS PL002
Medici	Fabrizio	ORG OR071
Medves	Marco	FIS OR061
Melchior	Andrea	TEC KN004
Melinte	Gheorghe	ANA OR023
Memboeuf	Antony	MAS PL005
Mendolicchio	Marco	TEO OR026
Meninno	Sara	ORG PZ011
Merlo	Francesca	ANA OR110
Mero	Angelica	ORG OR112
Messa	Francesco	ORG OR072
Messina	Grazia	FIS OR007
Messore	Antonella	FAR OR038
Metrangolo	Pierangelo	ORG PZ003
Mezzetta	Andrea	ORG OR062
Mezzomo	Lorenzo	ELE OR63
Micalizzi	Giuseppe	ANA OR111
Miceli	Mariachiara	TEC OR024
Micheletti	Cosimo	IND OR043
Miglio	Vanessa	FIS OR036
Miglione	Antonella	ANA OR046
Migliorati	Valentina	FIS OR121
Migliore	Rossella	ANA OR093
Milanese	Chiara	FIS OR026
Miletto	Ivana	FIS OR062
Milite	Ciro	FAR PZ001
Minella	Marco	ANA OR011
Minero	Claudio	ANA PL001
Minguzzi	Alessandro	ELE KN15
Minnelli	Cristina	ORG OR045
Mocci	Rita	ORG OR066
Moedlinger	Marianne	FIS OR125
Monaci	Linda	MAS KN002
Monciatti	Elisabetta	ORG OR113
Mondello	Luigi	ANA PZ002
Monica	Fabrizio	TEC KN002
Montalbano	Marco	FIS OR114
Montali	Laura	ANA OR125
Montero	Jorge	ELE OR09
Montesarchio	Daniela	ORG PZ006
Montini	Tiziano	IND OR041
Montone	Carmela Maria	ANA OR002
Morandi	Sara	FIS OR077
Moretta	Alma	DID OR006
Morillas Becerril	Lucía	ORG OR046
Moro	Miriam	ELE OR22
Mosconi	Edoardo	INO PZ010
Mostoni	Silvia	INO OR073
Motta	Stefano	TEO OR019
Moyano	Encarnación	MAS PL004
Mulas	Gabriele	FIS OR037

Munzi	Gabriella	TEC OR032
Mura	Monica	FIS OR020
Muraglia	Marilena	FAR OR027
Murgolo	Sapia	ABC OR040
Musazzi	Umberto	TFA OR018
Muscolino	Emanuela	TEC OR047
Musella	Simona	FAR OR005
Musolino	Maria Grazia	IND OR037
Mussini	Patrizia	ANA OR047
Mussini	Patrizia	ELE KN01
Mustorgi	Eleonora	ANA OR133
Musumeci	Francesca	FAR OR003
Nacci	Angelo	ORG OR139
Nale	Angeloclaudio	ELE OR46
Nannuzzi	Chiara	FIS OR112
Nardelli	Francesca	ABC OR012
Nardiello	Donatella	ANA OR012
Narzi	Daniele	TEC OR034
Navacchia	Maria Luisa	ORG OR047
Naviglio	Daniele	ANA OR112
Neese	Frank	INO PZ001
Negri	Fabrizia	TEO KN003
Neri	Giulia	ORG OR055
Nervi	Carlo	INO OR017
Nieto Fabregat	Ferran	ORG OR048
Nomellini	Chiara	FIS OR089
Nori	Valeria	ORG OR065
Notaro	Anna	ORG OR049
Oliva	Eleonora	ANA OR054
Oliveri	Valentina	CSB OR024
Olivieri	Diego	INO OR082
Olivo	Giorgio	ORG OR090
Operamolla	Alessandra	ORG OR056
Orian	Laura	FIS OR100
Orlandi	Manuel	ORG PZ010
Ostacolo	Carmine	FAR OR007
Pagano	Rita	CSB OR020
Pagot	Gioele	ELE OR47
Palazzi	Sergio	DID OR009
Palazzi	Sergio	DID OR014
Palmieri	Sara	ANA OR083
Palmioli	Alessandro	ORG OR050
Panniello	Annamaria	FIS OR050
Panza	Nicola	INO OR013
Paolantoni	Marco	FIS OR116
Paone	Emilia	IND OR038
Papa	Veronica	IND OR069
Pappalardo	Valeria	IND OR055
Pargoletti	Eleonora	ELE OR58
Parmeggiani	Camilla	IND OR030
Parnigotto	Mattia	ELE OR13

Parodi	Adriano	ORG OR030
Parrino	Francesco	TEC OR015
Pascale	Raffaella	MAS OR013
Pasini	Mariacecilia	ORG OR052
Passarini	Fabrizio	ABC KN002
Pastore	Andrea	ANA OR126
Patamia	Vincenzo	ORG OR053
Pavan	Cristina	INO OR003
Pavlos	Nikolaou	ELE OR42
Pavone	Michele	ELE KN64
Pecoraro	Adriana	FIS OR059
Pecoraro	Tania	INO OR034
Peddis	Davide	DID OR007
Peddis	Davide	FIS OR003
Pedone	Alfonso	TEO KN002
Pedrazzani	Riccardo	INO OR046
Pedretti	Silvia	MAS OR002
Pelagatti	Paolo	INO OR053
Pellegrino	Francesco	ANA KN003
Pelosi	Chiara	FIS OR119
Penconi	Marta	FIS OR057
Perathoner	Siglinda	IND KN008
Perego	Carlo	IND KN005
Perinelli	Diego	TFA OR015
Perrella	Fulvio	TEO OR027
Perrone	Daniela	ORG OR051
Peruffo	Nicola	FIS OR046
Petralito	Stefania	TFA OR004
Petri	Elisabetta	ELE OR02
Petrone	Alessio	TEO OR012
Pettazzoni	Luca	ORG OR057
Phan Huu	Andrea	TEO OR032
Piacentini	Emma	TFA OR005
Piacenza	Elena	FIS OR023
Picca	Rosaria Anna	ANA OR066
Picci	Giacomo	INO PZ003
Piccinni	Marco	ELE OR04
Piga	Isabella	MAS OR003
Pigani	Laura	ANA OR048
Pinto	Gabriella	ANA OR013
Pintus	Anna	INO OR044
Pinzi	Luca	FAR OR029
Piovano	Alessandro	FIS OR051
Piovano	Alessandro	IND OR025
Piovesana	Susy	ANA IL001
Pipitone	Giuseppe	IND OR022
Pippione	Agnese	FAR OR001
Pirali	Tracey	FAR KN003
Piras	Federica	ABC OR041
Pirola	Carlo	IND OR068
Pironti	Concetta	ABC OR042

Pirota	Valentina	ORG OR100
Pirro	Fabio	INO PZ006
Pisani	Michela	CSB OR017
Pisani	Silvia	TFA OR021
Pither	Molly	ORG OR092
Platella	Chiara	CSB OR012
Plutino	Maria Rosaria	FIS OR087
Podda	Edoardo	IND OR026
Poggi	Giovanna	FIS OR075
Poli	Federico	ELE OR27
Polo	Annalisa	ELE IL32
Polo	Annalisa	FIS OR032
Ponte	Fortuna	INO PZ004
Porpora	Francesca	ABC OR030
Porto	Michele	FIS OR095
Pota	Giulio	TEC OR013
Potenti	Simone	ORG OR101
Pratesi	Debora	ORG OR093
Prati	Silvia	DID OR013
Pravatto	Pierpaolo	TEO OR033
Prejanò	Mario	INO OR059
Prete	Prisco	IND OR046
Previti	Santo	FAR OR025
Prosa	Mario	FIS OR084
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Nardiello	Donatella	ANA P0064
Nardiello	Donatella	ANA P0065
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Negro	Enrico	ELE P0011
Nicosia	Angelo	IND P0021
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Notardonato	Ivan	ANA P0087
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Pavoni	Elena	ANA P0014
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Pellis	Giulia	ABC P0006
Pepe	Angela	MAS P020
Pepe	Giacomo	FAR P0034
Perego	Jacopo	IND P0023
Perra	Matteo	TFA P0022
Peruffo	Nicola	FIS P0049
Petrilli	Marzia	ORG P0084
Pianta	Nicolò	ELE P0014
Pierini	Adriano	TEO P0004
Pierri	Martina	ORG P0085

Pietracci	Lorenzo	INO P0064
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Pirodda	Gabriele	TEC P0017
Pirola	Carlo	IND P0026
Pisano	Luisa	ORG P0087
Pittalà	Valeria	FAR P0055
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Pogni	Rebecca	FIS P0051
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Rossi	Ruggero	IND P0031
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Saliu	Francesco	ABC P0011
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